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CIII.—ON THE CONVERSION OF METHYLPYROMUCIC ACID INTO ALDEHYDOPYROMUCIC AND DEHYDROMUCIC ACIDS.[1]

BY H. B. HILL AND H. E. SAWYER.

The structure of methylfurfurol was established with sufficient precision by Maquenne[2] through its preparation from rhamnose, and this structure was afterward confirmed by Hill and Hendrixson[3], who converted the corresponding methylpyromucic acid into the acetacrylic acid of Wolff[4] by oxidation with bromine in aqueous solution. While the dehydromucic acid of Fittig and Heinzelmann,[5] from the method of its formation, must necessarily have an analogous structure, it seemed to us of interest to prove this relation experimentally by preparing the latter acid directly from methylpyromucic acid.

Hill and Jennings[6] had already described the ω-oxymethylpyromucic acid, but their experiments, as well as those which we made ourselves, convinced us that there was little hope of converting this acid smoothly into the corresponding dibasic acid by oxidation. Under all the conditions which we tried the furfuran ring was itself attacked, and no dehydromucic acid could be discovered among the products of the oxidation. As the furfuran ring is not readily opened by dry bromine, it seemed probable that we might accomplish our end by replacing two or three hydrogen atoms of the methyl group by bromine. Hill and Jennings had already found that the ω-brommethylpyromucic acid could be made without much difficulty by the action of bromine at high temperature, and we therefore attempted to introduce a second atom of bromine by the same method taking this acid as our starting-point. Although we succeeded in making enough of the ω-dibrommethylpyromucic acid to establish its identity by analysis, and to show that it could be converted into an aldehyde acid by the action of water, much more than the theoretical quantity of bromine was required, and the yield was so small that it would have been impossible for us to prepare in this way the material needed for a study of the aldehyde acid in question. We therefore turned to the chloranhydride of methylpyromucic acid, and found, as we had hoped, that it was so much more readily attacked by bromine than the free acid that it was not difficult in one operation to replace two of its hydrogen atoms by the action of no very large excess of bromine; in the course of the reaction the chlorine was also replaced by bromine so that the ω-dibrompyromucyl bromide was the product obtained. Although it was not easy to prepare this body in a pure condition, the crude product was formed in satisfactory quantity, and when this was heated with water it yielded the aldehyde acid which could be purified without difficulty.

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[1] The work described in the following paper was presented in the form of a thesis to the Faculty of Arts and Sciences of Harvard University in May, 1895, by Harris E. Sawyer, then candidate for the degree of Doctor of Philosophy.

[2] Compt. rend., **109**, 603.

[3] Ber. d. chem. Ges., **23**, 452.

[4] Ann. Chem. (Liebig), **264**, 245.

[5] Ber. d. chem. Ges., **9**, 1198.

[6] This JOURNAL, **15**, 181; Proc. Amer. Acad., **27**, 210.

The oxidation of the aldehydopyromucic acid to dehydromucic acid proved to be a simple matter. The statement of Heinzelmann[1] that argentic dehydromucate is blackened when boiled with water, made us hesitate to employ argentic oxide to effect the conversion. After we had found that several other oxidizing agents yielded dehydromucic acid in but small and varying quantities, we discovered that argentic oxide in alkaline solution brought about an almost quantitative oxidation. The dibasic acid thus formed was then easily shown to be identical with the dehydromucic acid prepared directly from mucic acid.

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[1] Ann. Chem. (Liebig), **193**, 190.

In the preparation of the methylpyromucic acid which was needed for this investigation we modified slightly the method recommended by Hill and Jennings in that we substituted sodic hydrate for the sodic carbonate which they used; and, furthermore, we added this at the outset, instead of waiting until the reduction of the argentic oxide was apparently complete. These modifications made the method more convenient in practice, enabled us to increase the quantity of material employed in each operation, and at the same time slightly increased the yield of the acid. For 30 grams of methylfurfurol we found it best to use about 75 grams of well washed argentic oxide and 11 grams of sodic hydrate dissolved in a liter of water. The argentic oxide was suspended in the dilute solution of sodic hydrate contained in a two-liter flask; after the mixture has been heated to boiling the methyl furfurol was added and the whole boiled under a reverse cooler for about half an hour. From 197 grams of methylfurfurol boiling at 184°-185° (uncorrected) we obtained in this way 212.6 grams of crude methylpyromucic acid, or 94.2 per cent. of the theoretical amount, so that the yield was nearly quantitative.

Methylpyromucyl Chloride, $C_6H_5O_2Cl$.—In the course of our work we prepared the chloranhydride of methylpyromucic acid, a body which has not yet been described. It may be made most conveniently by the action of a slight excess of phosphoric pentachloride upon the fused and powdered acid. The reaction usually sets in at once at ordinary temperature or after warming gently. It may also be made by the action of phosphorus trichloride upon the acid, a fact that is worthy of note since we have been unable to prepare pyromucyl chloride by the same reaction. Methylpyromucyl chloride is a colorless liquid which boils at 93°-94° under a pressure of 18 mm., and at 202° under a pressure of 756 mm. At low temperature it crystallizes in interlacing needles which melt at 28°. On standing a green color is developed. An analysis showed that it contained the proper percentage of chlorine.

0.3276 gram substance gave 0.3264 gram AgCl.

	Calculated for $C_8H_5O_3Cl$.	Found.
Cl	24.54	24.63

ω-Dibrommethylpyromucic Acid, $C_6H_4Br_2O_3$.—Hill and Jennings found that bromine at the boiling-point of chloroform attacked methylpyromucic acid mainly in the methyl group and formed the ω-brommethylpyromucic acid. It seemed, therefore, not improbable that further action under the same conditions might yield an acid containing two bromine atoms in the side chain. Since it had been found that the replacement even of the first hydrogen atom of the methyl group could not be brought about smoothly and required at least twice the theoretical quantity of bromine, it seemed advisable to prepare in the first place pure ω-brommethylpyromucic acid and submit this to the further action of bromine. We modified the method of preparation recommended by Hill and Jennings, only in that we allowed the reaction to proceed in direct sunlight, and used a concave mirror to increase the illumination. Under these conditions we found that the reaction proceeded much more rapidly, and that the yield was at the same time increased; we also took great pains to dry the material used and to exclude all moisture during the operation. We found, however, that twice the theoretical quantity of bromine must be used as before in order to obtain the best yield. All our experiments with ω-brommethylpyromucic acid were carried on in direct sunlight with the aid of a concave mirror. The acid was dissolved in several times its weight of chloroform, and bromine, somewhat diluted with chloroform, slowly added to the boiling solution. Substitution was slowly effected, and it was evident that the reaction was tolerably complex since at least six times the theoretical quantity of bromine was required. After the reaction was completed a part of the chloroform was removed by distillation and the brown viscous residue allowed to stand for some time *in vacuo* over lime. The crystals which separated were then drained on a porous plate, washed with cold ligroïn, and finally recrystallized from benzol with the addition of purified boneblack. The product thus obtained proved to have the composition required by a dibrommethylpyromucic acid.

I. 0.2000 gram substance gave 0.1884 gram CO_2, and 0.0307 gram H_2O.

II. 0.1281 gram substance gave 0.1692 gram AgBr.

	Calculated for $C_6H_4Br_2O_3$.	Found. I.	II.
C	25.36	25.69	....
H	1.42	1.72	....
Br	56.31	....	56.22

The ω-dibrommethylpyromucic acid crystallizes in small greenish-white prisms which melt at 153°. It is quite readily soluble in ether, chloroform, or benzol, very sparingly soluble in ligroïn, and almost insoluble in carbonic disulphide. It dissolves readily with decomposition on heating with alcohol or water ; in the latter case hydrobromic acid is formed in abundance, and the aqueous solution then contains a body which reduces argentic oxide and reacts with hydroxylamine and phenylhydrazine. This behavior warrants the conclusion that the two bromine atoms are attached to the carbon of the methyl group. The yield of the ω-dibrommethylpyromucic acid which we could obtain in this way was so extremely small that we made no attempt to prepare it in larger quantities, but tried at once to find a more advantageous method for making the corresponding aldehyde acid.

ω-Dibrommethylpyromucyl Bromide, $C_6H_3Br_3O_2$.—It is well known that the haloid anhydrides of the organic acids are much more open to substitution than the acids themselves ; it seemed to us probable, therefore, that we might be able to replace two hydrogen atoms of the methyl group in one operation by treating methylpyromucyl chloride with bromine at high temperature. We found on trial that the reaction ran quietly and smoothly, that a comparatively small excess of bromine was required, and that the yield was tolerably satisfactory. A study of the product soon showed, however, that the chlorine had also been replaced by bromine, so that the ω-dibrommethylpyromucyl bromide had been formed. As in the preparation of the ω-dibrommethylpyromucic acid already described we found that exposure to direct sunlight greatly facilitated the reaction. The methylpyromucyl chloride was heated in a small flask, fitted with a reverse cooler and drop-funnel, placed in a white porcelain dish containing sulphuric acid which was kept at 150°. The apparatus was placed in bright sunlight, and the light further concentrated upon the flask by means of a concave mirror. In practice we found that about 2.5 molecules of bromine were required to obtain the best results. At first the color of the bromine, as it was gradually added, immediately disappeared with the vigorous evolution of hydrobromic acid, but toward the end of the operation the action proceeded more slowly, and occasionally the color of the bromine was persistent before the whole amount had been added. The hydrobromic acid and the excess of bromine were then driven out by a current of dry carbonic dioxide, and the viscous product allowed to stand *in vacuo* over lime. It gradually solidified in part and the oily impurities could then be removed by means of porous earthenware plates. By repeated recrystallization from chloroform or ligroïn the substance may be further purified, but not without considerable loss of material.

I. 0.2242 gram substance gave 0.1730 gram CO_2, and 0.0230 gram H_2O.

II. 0.2345 gram substance gave 0.3810 gram AgBr.

III. 0.2012 gram substance gave 0.3254 gram AgBr.

	Calculated for $C_6H_3Br_3O_2$.	Found. I.	II.	III.
C	20.76	21.05	....	....
H	0.87	1.15	....	....
Br	69.15	....	69.14	68.82

ω-Dibrommethylpyromucyl bromide, when crystallized from chloroform or benzol, forms thin, elongated plates with pointed ends which melt at 102°; from ligroïn it crystallizes in granular aggregations. It dissolves readily in cold chloroform, benzol, or carbonic disulphide, more sparingly in cold ligroïn, but more freely on heating; on warming with alcohol or water it dissolves with decomposition.

Aldehydopyromucic Acid, $C_6H_6O_4$.—This acid can readily be made by the action of water upon the ω-dibrompyromucic bromide which has just been described. The complete purification of the acid bromide is attended with considerable loss of time and material; we have, therefore, found it much more advantageous to use for the preparation of the acid crude material thoroughly dried upon porous tiles. When heated with water the body melts and gradually goes into solution. In order to facilitate the reaction we found it convenient to pass in at the same time a current of steam, and noticed that the steam carried over a crystalline body rich in bromine, together with a minute amount of an acid, which could be extracted from the filtered distillate with ether. This acid, from the lack of material, we have been unable to study further, but we have identified the crystalline body as tetrabrommethane. It was readily soluble in ether, chloroform, benzol, carbonic disulphide, or ligroïn, melted at 92°–93°, and contained the proper percentage of bromine.

I. 0.1586 gram substance gave 0.3580 gram AgBr.

II. 0.1488 gram substance gave 0.3359 gram AgBr.

	Calculated for CBr_4.	Found. I.	Found. II.
Br	96.38	96.06	96.06

The aqueous solution left in the flask after distillation with steam was filtered, extracted with ether, and the crystalline residue left by the ether on distillation recrystallized from hot water with the addition of purified bone-black. The acid separates from the aqueous solution either in irregular, curved plates, which are anhydrous, or in long, slender needles, which contain one molecule of water; the anhydrous plates appear to be formed on cooling a hot concentrated solution, while the hydrous needles are formed by spontaneous evaporation at ordinary temperatures. The plates, when thoroughly dried by pressure, lose nothing in weight on exposure to the air, or over sulphuric acid.

0.1241 gram substance gave 0.2337 gram CO_2, and 0.0336 gram H_2O.

	Calculated for $C_6H_4O_4$.	Found.
C	51.42	51.38
H	2.88	3.03

The long needles effloresced rapidly when exposed to the air; for analysis they were dried by thorough pressure between folds of filter-paper.

I. 0.1528 gram substance gave 0.2550 gram CO_2, and 0.0500 gram H_2O.

II. 0.6900 gram substance lost over sulphuric acid 0.0759 gram H_2O.

	Calculated for $C_6H_4O_4.H_2O$.	Found.	
		I.	II.
C	45.56	45.52	....
H	3.82	3.66	....
H_2O	11.40	....	11.00

The dehydrated acid gave the following results:

I. 0.1370 gram substance gave 0.2594 gram CO_2, and 0.0367 gram H_2O.

II. 0.1456 gram substance gave 0.2735 gram CO_2, and 0.0389 gram H_2O.

	Calculated for $C_6H_4O_4$.	Found.	
		I.	II.
C	51.42	51.65	51.24
H	2.88	3.00	2.99

Aldehydopyromucic acid dissolves readily in alcohol, or hot water, more sparingly in ether; it is sparingly soluble in chloroform, and almost insoluble in benzol, ligroïn, or carbonic disulphide. When quickly heated it melts at 201°–202°, but if the temperature is slowly raised it sublimes with partial decomposition, and the residue melts at a higher temperature. On dry distillation it yields a liquid distillate, which gives a brilliant red color to aniline-acetate paper, showing that furfurol is thus formed with the loss of carbonic dioxide. We have succeeded in preparing no salts which invited further study. The barium salt was very soluble in water, and when precipitated from aqueous solution by the addition of alcohol it gave no satisfactory analytical results; the sparingly soluble silver salt gave no better results.

Phenylhydrazine Aldehydopyromucic Acid, $C_{12}H_{10}N_2O_3$.—When phenylhydrazine acetate is added to aldehydopyromucic acid dissolved in a solution of sodic acetate, the corresponding hydrazone separates in the form of clustered microscopic crystals. It is readily soluble in alcohol, more sparingly soluble in ether, and almost insoluble in benzol, chloroform, or carbonic disulphide; it dissolves immediately in dilute sodic hydrate, and is then reprecipitated by the addition of acids. When quickly heated it melts with decomposition at 176°.

0.1375 gram substance gave 14.9 cc. moist nitrogen at 17° and under a pressure of 768 mm.

	Calculated for $C_{12}H_{10}N_2O_3$.	Found.
N	12.20	12.65

Under somewhat different conditions we obtained a product which contained a higher percentage of nitrogen, but we have made no further study of it.

Oxime of Aldehydopyromucic Acid, $C_6H_5NO_4$.—When hydroxylamine hydrochlorate is added to a concentrated solution of sodic aldehydopyromucate, the separation of the oxime at once begins, and the reaction is soon completed. The granular precipitate can readily be purified by recrystallization from boiling water.

I. 0.2020 gram substance gave 0.3432 gram CO_2, and 0.0629 gram H_2O.

II. 0.1500 gram substance gave 12.4 cc. moist nitrogen at 25°.6 and under a pressure of 746 mm.

	Calculated for $C_6H_5NO_4$.	Found.	
		I.	II.
C	46.43	46.34	....
H	3.25	3.48	....
N	9.06	....	8.98

The oxime is readily soluble in alcohol or ether, but is insoluble in benzol or chloroform; it dissolves freely in boiling water, and as the solution cools the greater part separates unchanged. Even when heated with water in a sealed tube to 150° but trifling decomposition ensues; hydrochloric acid, however, decomposes it rapidly on heating, and hydroxylamine is formed. In a capillary tube it is slowly decomposed, but if rapidly heated it melts with decomposition at 224°–226°.

Dehydromucic Acid, $C_6H_4O_5$.—Aldehydopyromucic acid may be converted into dehydromucic acid almost quantitatively by warming a solution of its sodium salt containing an excess of sodic hydrate with freshly precipitated argentic oxide. The filtered solution is concentrated, acidified with hydrochloric acid, and the dehydromucic acid which separates well washed with cold water. We found that dehydromucic acid could also be formed by the action of several other oxidizing agents in alkaline solution, but the yield was unsatisfactory. In the course of our work we noticed that an alkaline solution of the aldehyde acid is slowly oxidized by exposure to the air. The dehydromucic acid made by the action of argentic oxide appeared to be identical with that prepared from mucic acid by heating it with a mixture of concentrated hydrobromic and hydrochloric acids according to the method of Klinkhardt.[1] It was sparingly soluble in water, still less soluble in alcohol, sublimed in a capillary tube without melting, and gave the reaction with ferric chloride which is described by Klinkhardt as characteristic. When dried over sulphuric acid it gave the following results :

0.1608 gram substance gave 0.2697 gram CO_2, and 0.0407 gram H_2O.

	Calculated for $C_6H_4O_5$.	Found.
C	46.15	45.75
H	2.58	2.83

The identity of the acid was further established by an analysis of the barium salt, which, according to Heinzelmann[2] and Seelig[3] contains 2½ molecules of water. We found that the salt crystallized in slender, colorless needles, which were permanent in the air, but slowly effloresced over sulphuric acid.

0.6730 gram air-dried salt at 200° lost 0.0900 gram H_2O.

	Calculated for $BaC_6H_2O_5.2\frac{1}{2}H_2O$.	Found.
H_2O	13.38	13.37

0.5830 gram salt dried at 200° gave 0.4658 gram $BaSO_4$.

	Calculated for $BaC_6H_2O_5$.	Found.
Ba	47.15	47.03

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[1] J. prakt. Chem., (2). **25**, 43.

[2] Ann. Chem. (Liebig), **193**, 189.

[3] Ber. d. chem. Ges., **12**, 1085.

CIV.—ON THE 3,4,5-TRIBROMANILINE AND SOME DERIVATIVES OF UNSYMMETRICAL TRIBROMBENZOL.[1]

BY C. LORING JACKSON AND F. B. GALLIVAN.

In the course of an attempt to prepare the vicinal tetrabrombenzol, which unfortunately did not lead to the desired result, we had occasion to make the 3,4,5-tribromaniline, when to our surprise our product melted at 118°–119°, whereas Koerner, who discovered the substance, says of it, "non fondente a 130°, e che, a quanto pare, si scompone per un più forte riscaldamento."[2] As the statement quoted from Koerner contained all that was known of the properties of the substance, except that he says also that it forms salts, we have made a more careful study of this tribromaniline in order to characterize it. Our melting-point not only differed from Koerner's, but also was essentially identical with that of the ordinary tribromaniline $NH_2 1, Br_3 2,4,6$—which melts at 118° according to Koerner, at 119°–120° according to Fittig and Buchner. It was necessary, therefore, in the first place to prove that our substance was the tribromaniline $NH_2 1, Br_3 3,4,5$, even although from our knowledge of the positions usually taken by bromine atoms on the benzol ring it seemed hardly possible that a body formed by the action of bromine on paranitraniline could have a different constitution. To make the proof absolute we eliminated the amido group from our tribromaniline, when we found that the vicinal tribrombenzol melting at 87° and crystallizing in tables was formed with remarkable ease. It follows, therefore, that Koerner's statement that the tribromaniline ($NH_2 1, Br 3, Br 4, Br 5$) does not melt even at 130° is incorrect, and that it melts at 118°–119°. We have added to the description of the compounds of this tribromaniline which follows an account of some other substances obtained in our attempts to make vicinal tetrabrombenzol, and also a few corrections and additions to our paper "On Some Derivatives of Unsymmetrical Tribrombenzol"[1] published somewhat more than a year ago.

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[1] Presented to the American Academy of Arts and Sciences, May 12, 1897.

[2] Gazz. Chim. Ital., 1874, 409.

3,4,5-Tribromaniline, $C_6H_2Br_3NH_2$.

To prepare this substance[2] paranitraniline was suspended in water, and converted by the addition of bromine into dibromparanitraniline. Then 50 grams of this product were mixed in a flask with hydrobromic acid (boiling at 125°), and sodic nitrite added in excess. After the last portion of the nitrite had been decomposed, a large excess of hydrobromic acid was added, and the contents of the flask allowed to stand over night. The diazo compound formed was then decomposed by heating on the steam-bath, and the tribromnitrobenzol obtained was reduced with tin and hydrochloric acid without any previous purification, when most of the tribromaniline separated in the solid state, although a small amount could be recovered from the hydrochloric acid solution. It was purified by crystallization from alcohol or hot ligroïn.

Properties.—It crystallizes from alcohol and water in slender white needles, rather short and pointed at both ends. Although it crystallizes in needles like the ordinary tribromaniline, it differs from that in habit, as we could not succeed in obtaining very long needles similar to those which are so characteristic of the NH_2 1, Br 2, Br 4, Br 6 isomer. It melts between 118° and 119°, while the highest melting-point given for the isomeric form is that of Fittig and Buchner, 119°–120°. It is soluble in ether, chloroform, benzol, acetone, or alcohol; slightly soluble in cold, soluble in hot ligroïn; essentially insoluble in water. Dilute alcohol or hot ligroïn is the best solvent for it. It forms salts more readily than the $NH_2$1, $Br_3$2,4,6 tribromaniline, and a little less readily than the $NH_2$1, $Br_3$2,4,5-tribromaniline.[3] With bromine it gives pentabromaniline. By the elimination of its amido group it is converted into the vicinal tribrombenzol melting at 87°.

Chloride of Tribromaniline, $NH_2$1, $Br_3$3,4,5.

This salt could be made by boiling the tribromaniline with a large excess of concentrated hydrochloric acid, but was prepared for analysis by the more convenient method of dissolving the tribromaniline in benzol and adding a strong solution of hydrochloric acid[1] when the salt was precipitated.

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[1] This Journal, 18, 238.

[2] Koerner: Gazz. Chim. Ital., 1874, 347, 390.

[3] This Journal, 18, 247.

0.4976 gram of the salt gave, after the base had been removed by ammonic hydrate, 0.1911 gram of argentic chloride.

	Calculated for $C_6H_2Br_3NH_3Cl$.	Found.
Chlorine	9.69	9.50

Properties.—The salt crystallizes unaltered in white needles from hot water to which a few drops of hydrochloric acid have been added; but if it is boiled with water alone, it undergoes a partial decomposition. The salt is, therefore, much more stable than the chloride of the $NH_2 1, Br_3 2,4,6$-tribromaniline, which is decomposed completely by water. It is slightly soluble in benzol; insoluble in ligroïn or ether.

Bromide of Tribromaniline, $NH_2 1, Br_3 3,4,5$.

This salt was made by adding a strong aqueous solution of hydrobromic acid to 2 grams of the tribromaniline dissolved in benzol. The white precipitate formed was filtered out, washed with benzol, dried, and analyzed with the following result:

0.3841 gram of the salt gave, after the base had been precipitated with ammonic hydrate, 0.1771 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NH_3Br$.	Found.
Bromine	19.47	19.63

The bromide resembles the chloride in its properties, and, although slightly more unstable, is still much more stable than the bromide of the tribromaniline, $NH_2 1, Br_3 2,4,6$.

Sulphate of Tribromaniline, $NH_2 1, Br_3 3,4,5$.

To prepare this salt 3 grams of the tribromaniline were heated with moderately strong sulphuric acid. The tribromaniline soon dissolved, and on cooling the solution deposited fine large plates of the sulphate, which were purified by recrystallization from water slightly acidified with sulphuric acid, dried, and analyzed with the following result:

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[1] In order to obtain the chloride of the $NH_2 1, Br_3 2,4,6$-tribromaniline, gaseous hydrochloric acid must be used.

0.4671 gram of the substance, after treatment with ammonic hydrate, gave 0.1417 gram of baric sulphate.

	Calculated for $(C_6H_2Br_3NH_2)_2H_2SO_4$.	Found.
SO_4	12.66	12.49

Properties.—The salt crystallizes from dilute sulphuric acid in broad, white, shining plates, which are soluble in water; but if its aqueous solution is heated, it decomposes partially into the tribromaniline and sulphuric acid. In the presence of a little sulphuric acid, on the other hand, the aqueous solution can be heated without decomposition. The salt is soluble in alcohol, and its solubility is increased by heat; insoluble in benzol, chloroform, or ether.

Tribromphenylurethane, $C_6H_2Br_3NHCOOC_2H_5$, $NH1, Br_3 3,4,5$.

This substance was prepared by boiling a benzol solution of 10 grams of the tribromaniline with eight grams of chlorcarbonic ethyl ester in a flask with a return condenser. After heating for five hours, as no more hydrochloric acid was given off, the mixture was allowed to cool, when crystals appeared, which were filtered out, and crystallized from dilute alcohol until they showed the constant melting-point 169°–170°. The substance was then dried at 100°, and analyzed with the following results:

I. 0.1915 gram of the substance gave 0.2708 gram of argentic bromide by the method of Carius.

II. 0.1771 gram of the substance gave 0.2473 gram of argentic bromide by the method of Carius.

	Calculated for $C_6H_2Br_3NHCOOC_2H_5$.	Found. I.	II.
Bromine	59.70	60.20	59.43

The $NH_2 1, Br_3 2,4,6$-tribromaniline gives no urethane under these conditions.

Properties.—This tribromphenylurethane crystallizes from a mixture of alcohol and water in thin white rhombic plates frequently with the acute angles bevelled by two other planes, making a very obtuse angle with the sides of the original rhomb. It melts at 169°–170°; and is easily soluble in alcohol, ether, benzol, or chloroform; essentially insoluble in cold ligroïn, soluble in hot. Strong hydrochloric acid in the cold has no apparent action on it. Strong nitric acid or strong sulphuric acid dissolves it, and the addition of water to the solution gives a white precipitate.

When the tribromphenylurethane was boiled with aniline under a reverse condenser, a substance was obtained, after removing the excess of aniline with dilute hydrochloric acid, which crystallized from alcohol in very long needles, melted at 235°, and contained no halogen. There was no doubt, therefore, that it was diphenylurea $(C_6H_5NH)_2CO$, and that the aniline had replaced both the ethoxy group of the ester and the tribromphenylimido group by phenylimido radicals.

Tribromacetanilid, $C_6H_2Br_3NHCOCH_3$,NH1,$Br_3$3,4,5.

Eight grams of the perfectly dry tribromaniline were mixed in small portions at a time with a large excess of acetic anhydride, and the dark-colored solution warmed on the steam-bath for a few minutes. The substance was then precipitated by pouring its solution into water, and purified by many recrystallizations from alcohol, after which it was dried at 100°, and analyzed with the following results:

I. 0.1817 gram of the substance gave 0.2756 gram of argentic bromide by the method of Carius.

II. 0.1114 gram of the substance gave 0.1691 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NHCOCH_3$.	Found.	
		I.	II.
Bromine	64.50	64.55	64.63

Properties.—This tribromacetanilid crystallizes from alcohol in white, slightly radiating brushes made up of very small needles, or in globular groups of needles looking like chestnut burs. It melts at 253°–254°. The tribromacetanilid, NH1,$Br_3$2,4,6, melts at 232° according to Remmers. Our acetanilid is soluble in benzol and in hot alcohol, but only slightly soluble in cold alcohol; soluble with difficulty in ether or chloroform; essentially insoluble in ligroïn. Sulphuric acid saponifies it only after long boiling. Fuming nitric acid converts it into the nitro compound described below.

Tribromnitroacetanilid, $C_6HBr_3NO_2NHCOCH_3$, $NH1$, $Br_33,4,5$, NO_22.

To prepare this substance 20 grams of the dry tribromacetanilid were added, in small portions at a time, to a quantity of nitric acid of specific gravity 1.50. As the reaction is vigorous, the flask must be cooled and shaken continually during the addition of the acetanilid. The solution thus obtained was poured into water, and the yellowish precipitate crystallized from a mixture of acetone and alcohol until it showed the constant melting-point 229°, when it was dried at 100° and analyzed with the following results:

I. 0.1485 gram of the substance gave 0.2009 gram of argentic bromide by the method of Carius.

II. 0.1624 gram of the substance gave 0.2194 gram of argentic bromide.

	Calculated for $C_6HBr_3NO_2NHCOCH_3$.	Found. I.	II.
Bromine	57.55	57.55	57.49

Properties.—This tribromnitracetanilid crystallizes from alcohol and acetone in white, well-formed crystals, belonging either to the hexagonal or orthorhombic system. When less well crystallized it forms long, very slender prisms terminated by a single plane at an oblique angle, or thick clumps of curving needles. It melts at 229°, and is easily soluble in acetone, soluble in alcohol, slightly soluble in benzol or ether, essentially insoluble in ligroïn. Sulphuric acid saponifies it in time, but this effect is produced much more easily by a strong solution of sodic hydrate.

Tribromnitraniline, $C_6HBr_3NO_2NH_2$, NH_21, $Br_33,4,5$, NO_22.

This substance was obtained by boiling 10 grams of tribromnitracetanilid with a strong solution of sodic hydrate. As the tribromnitracetanilid was saponified, the solution took on a deep reddish-brown color. When the reaction was complete, the solution was acidified with acetic acid, which threw down a brownish precipitate. This was filtered out and recrystallized from alcohol and chloroform until it showed the constant melting-point 130°, when it was dried at 100°, and analyzed with the following results :

I. 0.1912 gram of the substance gave 0.2864 gram of argentic bromide by the method of Carius.

II. 0.2006 gram of the substance gave 0.3017 gram of argentic bromide.

III. 0.2624 gram of the substance gave 18.1 cc. of nitrogen at a temperature of 19°.4 and a pressure of 761.2 mm.

	Calculated for $C_6HBr_3NO_2NH_2$.	Found. I.	II.	III.
Bromine	64.00	63.77	64.01	....
Nitrogen	7.47	....	....	7.93

Properties.—This tribromnitraniline crystallizes from alcohol in yellowish orange needles arranged in radiating groups. If the cooling is rapid, little circular masses of needles are formed. It melts at 130°, and is easily soluble in alcohol, ether, benzol, or chloroform ; essentially insoluble in ligroïn or in cold water ; slightly soluble in boiling water.

In the hope of converting the tribromnitraniline just described into a tribromnitrobenzol, from which the vicinal tetrabrombenzol might be obtained, we submitted it to the diazo reaction as follows : 14 grams of the tribromnitraniline were dissolved in boiling alcohol previously acidified with sulphuric acid, and 10 grams of powdered sodic nitrite added in small portions at a time. The mixture was then boiled for thirty minutes and allowed to stand over night at ordinary temperatures. Upon adding water a yellowish precipitate was formed, which, after recrystallization from alcohol, melted at 230°. An analysis indicated that the substance was the phenol $C_6HBr_3NO_2OH$, although the agreement between the percentage of bromine found and that calculated left much to be desired. (Calculated per cent. of bromine, 63.83. Found, 64.54.) Unfortunately, we did not have enough substance for more thorough purification ; but its properties showed plainly that it was a phenol, as it dissolved in a solution of sodic ethylate forming a reddish-brown salt, from which the original substance was recovered by acidification. As, therefore, this line of work evidently would not lead to the vicinal tetrabrombenzol, we did not think it worth while to undergo the large amount of labor necessary to prepare more of this phenol in order to characterize it more satisfactorily.

Tribromphenylurethane, $C_6H_2Br_3NHCOOC_2H_5$,NH1,$Br_3$2,4,5.

This substance was prepared in order to characterize more fully the tribromaniline $NH_2$1,$Br_3$2,4,5, described in our first paper.[1] 10 grams of the tribromaniline dissolved in benzol were heated with 8 grams of chlorcarbonic ethyl ester in a flask with a return condenser, until no more hydrochloric acid was given off. The product thus obtained was crystallized from alcohol, until it showed the constant melting-point 101°, when it was dried and analyzed with the following result:

0.1432 gram of the substance gave 0.2016 gram of argentic bromide by the method of Carius.

	Calculated for $C_6H_2Br_3NHCOOC_2H_5$.	Found.
Bromine	59.70	59.92

Properties.—This tribromphenylurethane crystallizes from alcohol and water in long, slender, white needles in radiating bunches, forming a thick felted mass. It melts at 101°, and is freely soluble in alcohol, ether, benzol, chloroform, or glacial acetic acid; insoluble in water. When it is heated with aniline it yields diphenylurea melting at 235°, and the tribromaniline, which was recognized by its peculiar odor. Its behavior, therefore, in this respect, is like that of the tribromphenylurethane NH1,$Br_3$3,4,6, previously described in this paper.

Tribromnitracetanilid, $C_6HBr_3NO_2NHCOCH_3$,NH1,$Br_3$2,4,5.

This substance was prepared from the corresponding acetanilid described in our previous paper.[2] We have not determined the position of the nitro group, but should suppose it would be ortho to the acetamido group, and therefore 6. 5 grams of the tribromacetanilid were added in small portions at a time to about 40 grams of nitric acid of specific gravity

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[1] This JOURNAL, **18**, 247.

[2] *Ibid*, **18**, 249.

1.50. The mixture was allowed to stand an hour at ordinary temperatures, and then poured into a large volume of cold water; the precipitate was recrystallized from alcohol until it showed the constant melting-point 228°, when it was dried at 100° and analyzed with the following result:

0.1001 gram of the substance gave 0.1348 gram of argentic bromide by the method of Carius.

	Calculated for $C_6HBr_3NO_2NHCOCH_3$.	Found.
Bromine	57.55	57.33

Properties.—This tribromnitracetanilid crystallizes from hot alcohol in little, branched needles, generally arranged in circular radiating groups, or in sheaves. It was pinkish white, but is probably white when perfectly pure. It melts at 228°, and is freely soluble in ether, benzol, chloroform, carbonic disulphide, or glacial acetic acid. Sulphuric acid, when boiled with it, converts it into the tribromnitraniline described below.

Tribromnitraniline, $C_6HBr_3NO_2NH_2$, $NH_2$1, $Br_3$2,4,5.

Ten grams of the tribromnitracetanilid were heated in a flask with a return condenser, with sulphuric acid diluted to the specific gravity 1.44, until the solid went into solution. The solution after it had cooled, was diluted with water, neutralized with dilute sodic hydrate, and the brownish precipitate purified by recrystallization from alcohol. When it showed the constant melting-point 130°, the substance was dried at 100°, and analyzed with the following result:

0.2341 gram of the substance gave 0.3513 gram of argentic bromide by the method of Carius.

	Calculated for $C_6HBr_3NO_2NH_2$.	Found.
Bromine	64.00	63.87

Properties.—This tribromnitraniline crystallizes in rather thick yellow needles, often united longitudinally, and sometimes very much branched. It melts at 130°, and is very soluble in ether, benzol, chloroform, acetone, ligroïn, or carbonic disulphide; soluble in alcohol; soluble with difficulty in hot water.

Behavior of Tribromdinitrobenzol ($Br_3 1,2,4(NO_2)_2 3,5$) *with Sodic Ethylate.*

This reaction was described in our previous paper,[1] but, unfortunately, in determining the composition of the principal product, we relied only on a bromine determination. On returning to the subject we realized that this was entirely insufficient to settle the nature of the body, since the ethoxy group has nearly the same molecular weight, 45, as the nitro group, 46, and therefore our bromine determination would serve equally well for a tribromresorcine (the composition which we had assigned to it, percentage of bromine 59.55), or for a tribromnitrophenetol (percentage of bromine 59.40). We accordingly prepared some more of the substance and tested for nitrogen, when to our great mortification we found that it was present, and that the substance therefore is tribromnitrophenetol, and not tribromresorcine. We regret exceedingly that our carelessness should have introduced this mistake into the chemical literature. Its composition was definitely settled by the following analyses :

I. 0.2430 gram of the substance gave 0.3407 gram of argentic bromide by the method of Carius.

II. 0.3797 gram of the substance gave 11.9 cc. of nitrogen at a temperature of 26° and a pressure of 766.5 mm.

	Calculated for $C_6HBr_3NO_2OC_2H_5$.	Found.	
		I.	II.
Bromine	59.40	59.67	....
Nitrogen	3.47	....	3.51

Properties of Tribromnitrophenetol.—These were given in our first paper as the properties of tribromresorcine ; we therefore think it best to repeat them here under the true name. It crystallizes from alcohol in long, white, pearly plates terminated by two planes at an acute angle, which is usually truncated by a basal plane. It melts at 158°. It is nearly insoluble in cold alcohol, soluble in hot ; soluble in chloroform, benzol, or acetone ; slightly soluble in cold ligroïn, more soluble in hot. The best solvent for it is hot alcohol.

In the aqueous filtrate from the tribromnitrophenetol we found the salt of a diatomic phenol melting at 67°, to which, in our previous paper, we assigned the formula $C_6HBr(NO_2)_2(OH)_2$, on the ground of a bromine determination. In returning to the subject we thought it well to obtain more analytical data in regard to it, and for this purpose we have made and analyzed the barium salt.

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[1] This JOURNAL, 18, 244.

Barium Salt of Bromdinitroresorcine(?), $C_6HBr(NO_2)_2O_2Ba$.

The constitution of the phenol has not been proved; but, as according to analogy the two hydroxyls should be in the meta position to each other, we have adopted the name given above provisionally.

The barium salt was prepared as follows: 2 grams of the phenol were mixed with a freshly prepared alcoholic solution of sodic ethylate, and then treated with an aqueous solution of baric chloride. The yellow precipitate thus obtained was filtered as quickly as possible, washed three times with a little cold water, and once with ether, and then dried at 130° and analyzed with the following result:

0.2580 gram of the salt gave 0.1464 gram of baric sulphate.

	Calculated for $C_6HBr(NO_2)_2O_2Ba$.	Found.
Barium	33.09	33.36

This analysis, therefore, confirms our previous view of the composition of the phenol.

Properties.—The barium salt is an orange-yellow powder with no well defined crystalline form. When heated in the flame of a Bunsen lamp it explodes. It is soluble in water, and its solubility is increased by heat; slightly soluble in alcohol; insoluble in ether, chloroform, or ligroïn. Acids set free the phenol $C_6HBr(NO_2)_2(OH)_2$ from it.

CV.—A CONVENIENT GAS GENERATOR, AND DEVICE FOR DISSOLVING SOLIDS.

By Theodore William Richards.

Since the days when Priestley and Cavendish evolved their oxygen and hydrogen from very simple apparatus, many scores of contrivances for accomplishing the same end have burdened the pages of chemical periodicals. Among these many contrivances, the patient reader may find an apparatus to suit almost any particular exigency ; but most of the suggestions are unsatisfactory in at least one of the following respects. The apparatus suggested is apt to be either excessively complex, inconveniently brief in its time of effective action, or very inconstant as to the pressure of the gas delivered. In avoiding the last two faults, the suggester has usually run into the first, which does not always trouble the inventor as much as it does the user of the invention.

Perhaps the best of the many usual forms of apparatus, when large quantities of gas are desired, is that in which the liquid is allowed to fall drop by drop upon the solid, the saturated liquid being drawn off at the bottom.[1] The chief disadvantages of this apparatus are that a stop-cock regulated for delivering very small amounts of liquid is apt to be clogged by accidental obstruction ; that it is hard to regulate the drops of liquid so as to produce just the desired flow of gas ; and that the outflow of the partly exhausted but usually unsaturated liquid is apt to produce serious changes in the pressure of the gas, even if this outflow is arranged automatically. A simple apparatus which could supply fresh acid when needed and only when needed, and at the same time could carry off the refuse automatically without change of pressure, would evidently be a desirable improvement.

No startlingly new principle is to be expected in a new device to accomplish these ends, and none will be found in the apparatus described below. The idea of using the heavier specific weight of the exhausted solution in order to remove it and give place to the fresh supply, has been used by many experimenters,[2] and indeed Wollny, Sleenbuch, and Reatz have described apparatus similar in principle to the one independently invented to supply a long-felt need in this laboratory. The chief gain of the present apparatus is its great simplicity, which places it within the reach of every one, even the elementary student.

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[1] Seidler : Chem. Centrbl., 1884, 98 ; Gawalovski : *Ibid*, 1885, 369 : Breyer : *Ibid*, 1889 (2), 627 ; Ostwald : Ztschr. anal. Chem., 1892, 183 ; Mirus : Chem. Centrbl, 1894, (1), 706 ; N. Teclu, Ztschr. anal. Chem., 1894, 441, etc. Ostwald's apparatus is probably the best of these ; but in it the pressure is very inconstant.

[2] Wollny : Ztschr. anal. Chem., 1885 (Vol. 24), 214 ; Sleenbuch ; J. prakt. Chem., 1887 (Vol. 35), 364 ; Burgmeister : Chem. Centrbl., 1890, (1), 626 ; Raikow : *Ibid*, 1891, (1), 522 ; Reatz : Ztschr. anal. Chem., 1892, 415 ; Kalecsinsky : Chem. Centrbl, 1892, (2), 1058 ; Harris : J. Am. Chem. Soc., **17**, 809 ; Völler : Chem. Centrbl, 1896, (1), 1153 ; Norton : J. Am. Chem. Soc., **18**, 1057 : Andrews : Chem. Ztg., 1897, 667.

The accompanying sketches speak for themselves. The vessel containing the solid reagent is suspended half-way in a tall jar containing the liquid, in such a way that the heavy solution produced by the reaction is removed by a long tube reaching quite to the bottom of the jar. The fresh liquid is drawn up through a tube extending several centimeters into the heart of the generator (Figs. 1, 3, 4, and 5), or else supplied through small holes high up in its walls (Fig. 2). This method of supplying new reagent is the chief respect in which the present apparatus differs from previous ones; by its aid the fresh material is kept almost uncontaminated by the exhausted solution. Thus the circulation continues long unimpaired, and hence the evolution of gas remains remarkably constant. The pressure of the gas thus supplied is determined by the difference between the level of the liquid at its point of delivery and that of the same liquid at its point of contact with the outside air. Since this distance is constant, and the specific gravity of the part of the solution in question does not vary throughout much of the use of the charge, the pressure also remains essentially constant. It is true that this constancy is obtained at the sacrifice of a part of the otherwise available height of the jar, but since tall cylinders are easily obtainable, this is no great objection. Moreover, if one uses the most satisfactory means of purifying and drying the gas—tall vessels filled with beads, which are moistened with a counter-current of purifying liquid,[1]—no great pressure is necessary. The tube containing the regulating stopcock should always be arranged horizontally, in order that it may not be clogged by accumulating liquid.

The degree of saturation of the used solution is of course influenced by the size of the lumps of solid, by the depth of layer of solid through which the liquid must pass, and by the rate of the gas current drawn off. If it has not been very nearly saturated at first, the partly used solution will be drawn through the generator again; but this time the gas will be evolved at a slightly less pressure, for the specific

[1] Proc. Am. Acad., 32, 68.

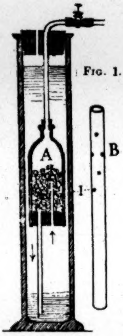
FIG. 1.

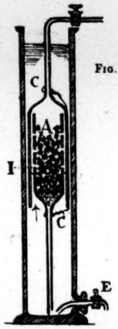
FIG. 2.

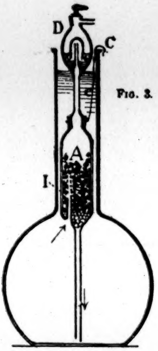
FIG. 3.

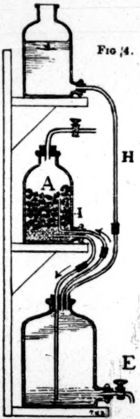
FIG. 4.

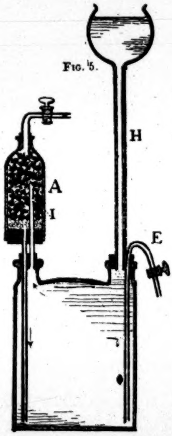
FIG. 5.

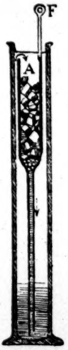
FIG. 6.

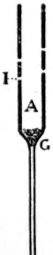
FIG. 7.

SECTIONAL DIAGRAMS OF GENERATORS AND DISSOLVER.

A = vessel for containing the solid. B = enlarged view of acid inlet tube.
C = wire for supporting or lifting the lower part of the apparatus.
D = drying apparatus to protect the gas stop-cock from condensed moisture.
E = stop-cock for withdrawing exhausted solution. F = handle. G = glass-wool.
By making the tube H flexible, the pressure may be altered at pleasure.
I = inlet holes for fresh solvent. In Fig. 7 these holes, large in size, may be loosely plugged with glass-wool.
Each piece of apparatus is more satisfactory if the solid is supported upon beads.
The arrows indicate the direction of the liquid current.

gravity of the liquid in its delivery tube has somewhat increased. It is surprising how sharply marked is the dividing line between the used and unused solutions in the jar below. Of course it is possible to draw off the saturated liquid at any time, by means of a siphon or tap at the bottom of the jar, replacing it by fresh liquid poured in above, without stopping the evolution of the gas.

Several forms of the generator are given below. That depicted in Fig. 1 has the advantage of ready construction from materials at everyone's command. Since the small rubber stopper is water-sealed, there is no danger of leakage, even with hydrogen. The small tube inside for delivering the liquid may advantageously be supplied with a few fine holes, as is shown in the enlarged detail at the right. The form shown in Fig. 2 may be employed when rubber must be eschewed, since it consists wholly of glass, the two parts being held together by a platinum wire. It is superior to the other in every respect except two: the solutions are not kept quite so sharply distinct, and the charging of the apparatus in the first place is a little more awkward. Neither of these objections is serious, however. It is sometimes advisable to use very dilute solutions of hydrochloric acid in the generator, because very dilute solutions yield a gas which is scarcely at all contaminated with acid. For this requirement, the arrangements shown in Fig. 3, 4, or 5 are well adapted. The third simply replaces the cylinder of the earlier forms by a long- and wide-necked flask, while the last consists of an easily made combination of a small bottle deprived of its bottom, a Wolff bottle, some tubes, and a bulb or funnel. The fourth is an obvious adaptation of the same idea. The fourth and fifth have the advantage of giving almost any pressure desired. In Nos. 3, 4, and 5, acid as dilute as normal may be used with success; hydrochloric acid of this strength yields a gas containing only about 0.002 milligram of chlorine per liter.

Since dissolved zincic sulphate of about 5.7 times normal strength, and ferrous sulphate of about 3.3 times normal strength, begin to crystallize at 10°, it is well not to use sulphuric acid of higher specific gravity than 1.18 or 1.10, respectively, when one of these two substances is to be a product of the reaction.

It is hoped that the ease of making and filling these simple pieces of apparatus, and the constancy of their operation, may commend them to the use of chemists, and cause them to supplant the clumsy, inconvenient, and inconstant apparatus of Kipp. By using two generators side by side, even the solid reagent may be renewed without interrupting the current of gas; and two of these generators are far easier to make than one of the complexity of Wollny's, the apparatus which comes nearest to accomplishing the same end.

These gas generators are naturally only of service when the residual solution is heavier than the initial solution. For the preparation of hydrochloric acid from salammoniac, where the exhausted solution is lighter than the strong sulphuric acid used, Wollny[1] has devised a suitable, although somewhat expensive, piece of apparatus. The same end may be accomplished by conveying off the exhausted liquid with the help of an inverted siphon, which will raise the lighter liquid from a lower to a higher level without interfering with the evolution of the gas. The viscosity of the solution, and its consequent frothing, so much complicate the manipulation of this siphon that it is not to be recommended for common use, however. Ordinarily a simple cylinder containing the sal ammoniac, immersed in a jar of acid, answers every purpose; because a momentary stoppage of the gas-current at once drives out the refuse, which rises to the top, and thus leaves room for fresh reagent. It is almost needless to add that a Kipp generator is very unsuitable for this purpose.

It is obvious that a device giving a saturated solution opportunity to remove itself by virtue of its increased weight may be used to conduct the rapid and automatic dissolving of crystals; and if the lower part of the receptacle for the solid is plugged with glass wool, the solution may be filtered while it is being made. Two forms of this device are shown in Figs. 5 and 6, the former being more easily made, and therefore more generally acceptable, while the latter is more satisfactory if the crystals contain impurities specifically lighter than the solution. To give an example of the working of this little instrument, whose underlying principle has undoubtedly been used by scores of chemists before, the following experiment may be cited: 30 grams of cupric sulphate placed in the "dissolver" required ninety minutes to dissolve in 200 cc. of water when no glass wool was used, and less than three hours when the solution was simultaneously filtered. The same weight of material in the same-sized crystals (averaging about 2 grams apiece) required fifteen days to dissolve in the same amount of water, at the same temperatue (20° ±), undisturbed in a beaker.

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[1] *Loc. cit.*

The "dissolver" cannot fail to be of value to the qualitative chemist who has many solutions to make, for it saves him the trouble of powdering his crystals and of filtering the solution after it is made; and the gas generator, from its wide applicability and simplicity, ought to be even more useful.

A REDETERMINATION OF THE ATOMIC WEIGHT OF ZINC.[1]

BY H. N. MORSE AND H. B. ARBUCKLE.

It has been shown by Richards and Rogers[2] that oxide of zinc derived from the nitrate, even when heated to very high temperatures, retains notable quantities of free nitrogen and free oxygen. The discovery of this hitherto unsuspected source of error in those determinations of the atomic weight of zinc which are based upon the weight of such oxide, made it necessary to revise the work of Morse and Burton.[3] The oxide which was obtained in the course of their work was not in condition to be utilized for the correction of the results; it was therefore decided to repeat the entire investigation and to determine as carefully as possible the amount of the gases retained by each specimen of the oxide. Fortunately, we still had a limited supply of the metal which had been prepared for the earlier determinations. This, as stated in the account of that work, had been prepared from Schuchardt's so-called

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[1] The work of which an account is given in this article was carried out under a grant from the Bache Fund (National Academy of Sciences).

[2] Proc. Am. Acad. Arts and Sciences, **28**, 200. [3] This JOURNAL, **10**, 311.

"absolutely chemically pure metallic zinc" by repeated distillation in a vacuum, and contained no impurities which could be detected by chemical or spectroscopic methods. Had it contained the alkalies or calcium, derived from the glass in which the distillations were made, as seems to be suggested by Richards and Rogers,[1] the fact would hardly have escaped detection when the metal was examined spectroscopically with Professor Rowland's ample facilities for refined work in that field. Furthermore, it may be stated that all parts of the zinc which had been in contact with the glass were removed with a file, it being assumed that whatever the metal acquired from the glass would remain near the surface of contact between the two.

The method of work, up to the point of determining the imprisoned gases, was an exact repetition of the procedure of Morse and Burton. Briefly stated, it consisted in converting the metal into nitrate in porcelain crucibles, and the nitrate into oxide by heating—moderately at first, but at last in a muffle furnace to a temperature sufficient to melt cast-steel.

Our arrangement for the liberation and collection of the occluded gases is represented in the accompanying figure. The tube *a* is something more than the normal barometric height in length, and of sufficient internal diameter to allow the crucibles containing the oxide to pass upward as the apparatus is exhausted; *b* is the reservoir for the dilute sulphuric acid which was used to dissolve the oxide; and *c*, the eudiometer in which the liberated gases were collected. The stop-cocks *d* and *e*, together with the adjacent portions of the glass tubes above and below them, were washed with a solution of mercuric chloride and immersed in mercury. The troughs for the mercury in which the stop-cocks were buried consisted of two parts, one of which fitted the back side of the apparatus at those points, and the other, the front. The two parts were held together by screws when in position. The spaces between the two halves of the troughs, and between the glass parts and the wood, were filled with an elastic gum, and the troughs were given supports which were independent of those which held the rest of the apparatus in position.

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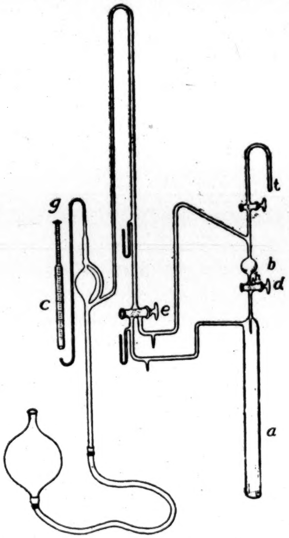
[1] Ztschr. anorg. Chem., 10, 2.

The eudiometer *c* was so narrow in the upper part that a millimeter division on the scale corresponded to only about 0.03 cc. It was, moreover, calibrated with great care. An acid containing about 28 per cent. of sulphuric acid was found to dissolve the oxide readily, and this concentration was therefore employed throughout the work. The bulb *b*, when half filled, contained enough of the acid for ten or a dozen determinations. The acid was introduced into the bulb and pumped out until, after standing for several days, no more gas could be obtained from it.



Having heated the oxide to constant weight in the muffle, the weighed pair of crucibles[1] were placed in a small crystallizing dish, and inserted in the open end of *a*. The mercury reservoir was then raised into position by means of screws and so adjusted that the lower edge of *a* rested evenly and firmly upon a piece of thick rubber packing in the bottom of the reservoir. Finally the mercury was introduced by means of a siphon and the apparatus exhausted, the height of the mercury in *a* being so adjusted in the end that the delivery tube for the acid reached nearly to the bottom of the crucible containing the oxide. As the mercury rose and the difference in pressure between the inner and outer sides of the tube increased, the table on which the reservoir rested was raised from time to time, by means of the adjusting screws in order to prevent *a* from sinking and thus bringing a strain upon the tubes connecting it with the pump.

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[1] See This Journal, 10, 316.

After exhausting and bringing the crucibles to the proper height with respect to the tube delivering the acid, the apparatus was allowed to stand undisturbed for twelve hours. If no leak developed within that time, the acid was admitted to the oxide. At the close of another period of from twenty to thirty hours, the gas liberated during the solution of the oxide was pumped into the eudiometer.

To determine the oxygen in the mixture of the gases, small quantities of hydrogen were introduced and exploded until no further decrease of volume occurred. Afterwards, electrolytic gas was repeatedly introduced and exploded in order to demonstrate the completeness of the removal of the oxygen. Before making a determination of oxygen, the hydrogen and the electrolytic gas to be used were tested as to their purity by exploding portions of the former with the latter, and portions of the latter by themselves and with air.

We deemed it of importance to inquire into two questions which affect the correctness of the results; the first is, whether the gas remaining after the removal of the oxygen is pure nitrogen; and the second is, whether any portion of the nitrogen remaining in the oxide at high temperatures is possibly in the form of a nitride. To settle the first, the gas residues were exploded with oxygen, to remove the excess of hydrogen, and afterwards examined for us spectroscopically in the physical laboratory of this university by Messrs. Ames and Humphreys. Aside from the substances known to be present—oxygen, water vapor, and nitrogen—nothing was found. The oxygen employed to remove the hydrogen, before submitting the gas for spectroscopic examination, was obtained by means of the apparatus recently described by Magruder,[1] which, on reversing the poles, gave us a gas containing less than 1 per cent. of hydrogen.

To satisfy ourselves regarding the very improbable presence of a nitride, we reserved the various solutions of the oxide; and, having determined the amount of sulphuric acid in measured portions of their mixture, we diluted to compensate for the concentration which the acid had suffered in the vacuum, and compared the solution with the original acid by means of the Nessler reaction. It was found that the minute quantity of ammonia originally in the acid had not increased during the solution of the oxide.

In the following table are presented the results of the eight successive determinations which were made after the apparatus and the method had been brought into satisfactory working condition. A larger number could not be made, owing to the limited supply of pure metal at our disposal. The weights given are corrected for air displacement; and liter volumes of oxygen and nitrogen, under standard conditions, are assumed to weigh here, as at latitude 45° and sea level, 1.42923 and 1.25461 grams, respectively. The error resulting from this assumption regarding the weights of the gases is, in our case, wholly insignificant, since a correction of their weights to the latitude and elevation of this place would have changed the result not more than a unit in the third decimal place.

The atomic weight calculated from the weights of the oxide, without correction for the occluded gas, namely 65.33, is higher than that of Morse and Burton, 65.27, by 0.06. Since Richards and Rogers have found that the quantity of the gas retained diminishes with increase of temperature, we conclude that the oxide must have been more highly heated in the latter than in the former series of determinations. We endeavored to maintain as exactly as possible all the conditions under which the former work was done; but it should be stated that the furnace employed by Morse and Burton was not available for our work, and the one used by us may have been somewhat more efficient, or the quality of the fuel may have been better. This difference of 0.06 corresponds to a difference of about 0.14 cc. of gas per gram of oxide. In other words, the oxide of Morse and Burton—probably owing to the lower temperature to which it was heated—retained approximately 0.14 cc. more gas per gram than ours.

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[1] This JOURNAL, **19**, 811.

	Weight of zinc.	Weight of oxide	Uncorrected atomic weight.	Volume of gas. (Standard conditions). cc.	Per cent. oxygen.	Corrected atomic weight. (O = 16)
I.	1.19573	1.48860	65.324	0.468	26.28	65.459
II.	1.03381	1.28707	65.312	0.402	18.14	65.445
III.	1.06519	1.32599	65.349	0.342	18.42	65.459
IV.	1.05802	1.31711	65.338	0.312	18.58	65.440
V.	1.26618	1.57619	65.348	0.521	13.82	65.489
VI.	1.03783	1.29198	65.336	0.408	35.28	65.475
VII.	1.08655	1.35276	65.307	0.412	19.55	65.437
VIII.	1.11364	1.38647	65.307	0.456	18.62	65.447
			Mean = 65.328			Mean = 65.457

11.02617 grams of the oxide yielded 3.321 cc. of gas, equivalent on the average to 0.301 cc. per gram of the material. It is noticeable that, while the proportions of the oxygen and nitrogen vary within wide limits—of the former from 13.82 to 35.28 per cent., and of the latter from 64.32 to 68.18 per cent.—the volumes of the two, taken together, are much more nearly constant. This will appear from the following table, which gives the volume of gas, per gram of oxide, for the individual determinations :

	Cc.
I.	0.314
II.	0.312
III.	0.258
IV.	0.237
V.	0.329
VI.	0.315
VII.	0.305
VIII.	0.329

The conclusion to be drawn from these relations is that reached by Richards and Rogers ; namely, that the phenomenon of gas occlusion is here due to physical causes solely.

There is, however, one inference drawn from the results of Richards and Rogers for which we find no confirmatory evidence in our data. It is, that the imprisoned oxygen escapes more readily than the nitrogen. In other words, that the proportion of oxygen diminishes with increasing temperature. If we grant that the total volume of occluded gas decreases with rising temperature, which cannot be disputed, also that the oxygen escapes more easily than the nitrogen, we arrive at conclusions which are not in accord with our results. In numbers III. and IV., for instance, the volumes of gas, per unit weight of the oxide, were the smallest—0.258 cc. and 0.237 cc. per gram of oxide, against an average of 0.301 cc.—indicating that the material in these cases had been heated to a higher temperature than in the others. We should, therefore, expect to find in them the smallest percentages of oxygen, but we do not. By the same course of reasoning we should conclude that in numbers V. and VIII., in which the largest volumes of gas were found, we ought also to find the largest percentages of oxygen; while, in reality, the proportion of that gas was, in VIII., not noticeably greater than in III. and IV., and in V. it was the least found in any of the determinations. Again, in numbers I. and VI. we should expect to find only a little more than an average proportion of oxygen, whereas they yielded much higher percentages than were found in any of the other cases. We must therefore conclude that the evidence at our command is altogether against the proposition, that the ratio of the retained gaseous constituents depends upon the temperature to which the oxide is heated. Indeed, if the retention is due to physical causes—to obstruction—it is difficult to understand why the oxygen should escape any more readily than the nitrogen.

As regards the final corrected result, 65.457, it is practically identical with the number 65.458, which is the value obtained from the results of Morse and Burton, when corrected according to the quantity of gas which Richards and Rogers[1] found to be retained by the oxide. It is also very near the number 65.459, which was obtained by Richards and Rogers[2] by the bromine method. It differs, however, from the result—65.404—of the later and more rigidly exacting determinations of Richards himself[3] by 0.053.

[1] Ztschr. anorg. Chem., **10**, 2.

[2] *Ibid.* **10**, 12.

[3] *Ibid.* **10**, 24.

It is to be regretted that the gas volumes to be dealt with in our work were so small, since a moderate error in measurement must produce a considerable effect upon the correction we were endeavoring to make. This difficulty was, of course, foreseen; and we tried to overcome it, as far as possible, by making the eudiometer very narrow, by repeated and painstaking calibrations, and by exercising care in the determination of temperatures and pressures. Under the circumstances we judge that the necessary errors connected with the gas analytical part of our work cannot have exceeded one per cent. of the correction which raised the apparent atomic weight from 65.33 to 65.46. But if these errors were cumulative throughout, instead of compensatory as they were more likely to be, the maximum effect upon the final result would be only a unit in the third decimal place.

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Contributions from the Chemical Laboratory of Purdue University.

DIRECT NITRATION OF THE PARAFFINS.

BY R. A. WORSTALL.

I.[1]

The literature relating to the action of nitric acid upon aliphatic hydrocarbons is very meagre. In general, the textbooks state that these hydrocarbons are either not attacked by nitric acid, hot or cold, or, if attacked, are completely oxidized to carbon dioxide and water.

Those who have been engaged in the study of petroleums, notably Pelouze and Cahours, Schorlemmer, Beilstein and Kurbatow, and Mabery, have noticed that nitric acid acts upon petroleum distillates. But that they regarded this action as taking place between the acid and hydrocarbons other than the paraffins, is shown not only by their published statements to that effect, but also by the fact that boiling these distillates with nitric acid has been recommended and used by each as an efficient means of removing these (supposed) foreign hydrocarbons, and thus of purifying the paraffins.

In general, it seems to have been assumed that the nitric acid acted upon naphthenes contained in the petroleum, but did not attack the paraffins. A striking example of this fact is found in the work of Beilstein and Kurbatow.[1] By boiling a 95°–100° *crude* fraction of American petroleum with four parts of nitric acid (specific gravity 1.38) until the acid was exhausted, they obtained a compound distilling at 195°–200°, and giving figures upon analysis fairly representative of nitroheptane. Apparently never suspecting its formation from heptane, they at once concluded that this American petroleum must contain *naphthenes*, and that this nitroheptane(?) was formed from one of the latter hydrocarbons. As a matter of fact, however, Mabery[2] has shown that American petroleums, in general, contain only very minute quantities of naphthenes.

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[1] Preliminary report.

Furthermore, Beilstein and Kurbatow state that the pure heptane obtained by distillation of this fraction after the treatment with nitric acid was scarcely at all attacked by fresh acid. In view of results now obtained, this point may be questioned.

A few investigators have noticed that oxidation results when paraffin hydrocarbons are boiled with nitric acid. Schorlemmer,[3] by the action of nitric acid of specific gravity 1.4 upon hexane, octane, and diamyl, obtained in each case carbonic and succinic acids along with other products which he did not identify, but which he thought to be nitrogen compounds. Beilstein and Kurbatow[4] observed the formation of acetic and succinic acids by the action of concentrated nitric acid upon a 95°–100° distillate of Caucasian petroleum.

Apparently the only work which has ever been done upon the direct nitration of the paraffins is that by Konowalow.[5] By heating normal hexane in sealed tubes to 130° with nitric acid of specific gravity 1.075, he obtained a yield of 30 per cent. of *secondary* nitrohexane. Similarly, from normal octane he obtained a *secondary* nitrooctane. Later,[6] by similar treatment of diisobutyl and diisoamyl he obtained from each the *secondary* and *tertiary* mononitro-compounds, and by acting upon the latter with more nitric acid, the *tertiary* dinitro-hydrocarbons were found. But *in no case* did he observe the formation of a *primary* nitro-hydrocarbon.

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[1] Ber. d. chem. Ges., **13**, 2029.

[2] This JOURNAL, **18**, 49.

[3] Ann. Chem. (Liebig), **147**, 214.

[4] Ber. d. chem. Ges., **13**, 1820.

[5] Compt. rend., **114**, 26.

[6] Ber. d. chem. Ges., **28**, 1852.

In a former paper[1] I have noted that heptane and octane are rather readily acted upon by nitric acid, and the preliminary results of an investigation of these reactions which is now in progress are here presented.

Preliminary Experiments.

As the method of boiling with nitric acid, or with mixed nitric and sulphuric acids, has long been employed as a means of purifying petroleum distillates, it seemed to me desirable to obtain some data relative to the action of the acid—especially to ascertain *the limit*, if any, to the reaction.

For a preliminary experiment, a quantity of so-called "sixty-three degree naphtha" was employed. This naphtha was thoroughly treated with an excess of fuming sulphuric acid, washed with caustic soda, and dried. Its specific gravity was then 0.7347 at 20°. It all distilled between 90° and 155° and appeared to consist chiefly of normal heptane and normal octane, with some nonane.

For the study of these reactions the following method has been employed in every case: A weighed quantity of the hydrocarbon is gently boiled with definite quantities of nitric acid, or of mixed acids, in a flask provided with a return condenser (and asbestos stopper) until red fumes of nitric tetroxide cease to be evolved, showing the nitric acid to be exhausted. The two layers are then, after cooling, separated mechanically, fresh acid added to the residual oil, and the treatment continued as long as is desired.

225 grams of the naphtha above described were treated in this way with a mixture of equal weights sulphuric and nitric acids with the following results:

Mixed acids. Grams.	Time. Hours.	Specific gravity of residue at 20°.
150	2	.....
150	2	0.7710
250	2	0.8150
250	4	0.8605
300	12	0.9210

That is, after *twelve hours' treatment*, and the use of about twice the calculated quantity of nitric acid, the naphtha, specific gravity 0.7347 at 20°, yielded 200 grams of a product whose specific gravity was 0.9210 at 20°.

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[1] This JOURNAL, 19, 836.

This residue, when washed and dried, could not be distilled, even under diminished pressure, without great decomposition and evolution of red nitric fumes, and evidently consisted of nitro-compounds. Not more than 200 cc. of unchanged naphtha was obtained by distilling this oil, and this was readily attacked by fresh acid.

Another portion of the naphtha was treated in the same way, save that the residual oil after each successive treatment with the mixed acids was completely extracted with strong sodium hydroxide to remove nitro-compounds. The nitration was then continued with the residual hydrocarbon. *No limit* could be found to the action of the acid, for the nitration continued up to the very last portion of the naphtha.

145 grams of the naphtha were next treated with nitric acid of specific gravity 1.40 in the same manner as described for the mixed acids, with the following results:

Acid. Grams.	Time. Hours.	Specific gravity of residue at 20°.
150	5	0.820
210	3	0.870
290	2	0.950

The residue amounted to 125 grams of the same nature as that obtained by the action of the mixed acids, and the naphtha, as nearly as could be determined, had been completely converted into these nitro-compounds.

In the same way it was proved that fuming nitric acid and dilute into acid (specific gravity 1.32, 1.23, 1.15) *completely transform* this naphtha into these nitro-products, the action of course varying in speed with the concentration of the acid, the products apparently being the same in each case.

From the results of these preliminary experiments it was evident that the paraffins were readily capable of direct nitration. In view of the great ease with which these nitro-compounds decompose upon distillation, it was determined to work with isolated hydrocarbons, studying the products in each case.

The hydrocarbons which have been used for the experiments herein described are the normal paraffins, hexane, heptane, and octane, from Pennsylvania petroleum. I desire to express my thanks to Dr. C. F. Mabery, of Case School of Applied Science, to whose kindness I am indebted for the material from which hexane was prepared, as well as for the pure heptane. The octane employed was fractioned from the naphtha previously described. In every case, the hydrocarbons have been completely treated with an excess of fuming sulphuric acid, boiled with sodium for several hours, and fractioned over sodium at 1° limits with the aid of Hempel columns, in no case less than twenty times, in one case thirty times, until a constant boiling-point was obtained for each hydrocarbon. Their boiling-points, specific gravity, and other properties have shown their purity.

Hexane, C_6H_{14}.

Normal hexane (boiling-point 68°.5–69°.5) specific gravity 0.6804 at 15°, has been found to be acted upon by fuming nitric acid, by nitric acid of specific gravity 1.42, and by mixed sulphuric and nitric acids, when gently boiled with these acids in an open flask with return condenser, but it is not acted upon to any appreciable extent by acid of greater dilution.

Fuming nitric acid gives the best results, the yield of nitro-products obtained by its use being satisfactory, and the hydrocarbon not being oxidized to any great extent. Usually, a yield of about 20 per cent. of crude nitro-products has been obtained by twenty hours' treatment with this fuming acid, with but little oxidation. But it is difficult, on account of the varying conditions of temperature in an open flask, to obtain concordant quantitative results.

To separate the nitro-products formed by the reaction, the layer of oil is separated from the spent acid, washed with water several times, and dried over calcium chloride. The unchanged hydrocarbon is then distilled off and again treated with more acid. In this way, by several days' successive treatments with fuming nitric acid, *hexane has been completely converted into nitro- and oxidation-products*, the yield of crude nitro-products amounting to perhaps 60 per cent. of the theoretical.

The residues of nitro-compounds left after distilling off the hexane are united and fractioned. Upon the first distillation considerable decomposition results with evolution of nitrogen tetroxide, and a tarry residue is left in the distilling-flask. This has been found to be due to dinitrohexane which cannot be distilled without decomposition. The separate fractions are again distilled, this time with but little or no decomposition.

This method of separation is unsatisfactory and wasteful, in that it destroys the dinitro-hydrocarbons, which usually amount to fully 50 per cent. of the total products. By steam distillation much better results are obtained, the mononitro-hydrocarbon, which is volatile in steam, being completely separated from the dinitro-hydrocarbon, which is not volatile in steam. But the first method was employed for the work herein described.

Nitrohexane, $C_6H_{13}NO_2$.

The distillates of nitro-products of hexane collect almost entirely at 180°-183°.[1] This distillate was thoroughly washed and dried and submitted to analysis.

By Dumas' method, 0.2062 gram substance gave 22.0 cc. (moist) nitrogen at 741 mm. and 23°.

	Calculated for $C_6H_{13}NO_2$.	Found.
N	10.72	10.93

Structure of Nitrohexane.—When treated with potassium hydroxide, potassium nitrite, and then with a few drops of sulphuric acid, it gave the intense red coloration of a nitrolic acid, disappearing with excess of acid, reappearing with the addition of more potassium hydroxide, characterizing it as *primary* nitrohexane.

About 5 grams were reduced to the amine by iron filings and dilute acetic acid, the reduction being complete in about a quarter of an hour. The solution was then made alkaline until sodium hydroxide and the liberated amine distilled off with steam. This hexylamine was a strong base which gave with alcoholic potash and chloroform the isonitrile reaction, and with carbon disulphide, alcohol, and solution of mercuric chloride, the mustard-oil reaction characterizing it as a *primary amine*.

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[1] The correct boiling-points, specific gravity, etc., of all these nitro-paraffins is now being investigated.

Analysis of the platinum double salt gave the following figures :

0.0110 gram substance gave 0.0034 gram platinum.

	Calculated for $(C_6H_{13}NH_3Cl)_2PtCl_4$.	Found.
Pt	30.47	30.90

Properties of Nitrohexane.—Nitrohexane is a light-yellow oil of a peculiar ester-like odor ; insoluble in water, readily soluble in alcohol, ether, etc., very sparingly soluble in aqueous solutions of caustic soda and potash, readily soluble in their alcoholic solutions with a red color.

Dinitrohexane, $C_6H_{12}(NO_2)_2$.

Occasionally, when separating the spent acid from the hydrocarbon, a middle layer has been noticed between the acid and the oil. This compound was separated, washed with water, and dried. Analysis gave the following figures :

By Dumas' method 0.3727 gram substance gave 55.0 cc. (moist) nitrogen at 741 mm. and 21° C.

By combustion, 0.1511 gram substance gave 0.2251 gram CO_2, and 0.0911 gram H_2O.

	Calculated.	Found.
C_6	40.90	40.65
H_{12}	6.82	6.67
N_2	15.91	15.94
O_4	36.37	36.74

These results leave no doubt concerning the composition of the oil.

Structure of Dinitrohexane.—While the quantity obtained was not sufficient to make a determination of its structure possible, there would seem to be no doubt, as its method of formation was exactly similar to that of dinitroheptane and dinitrooctane, that, like the latter, it is a primary nitro-compound, represented by the formula $CH_3(CH_2)_4CH(NO_2)_2$.

Properties of Dinitrohexane.—Dinitrohexane is a clear yellow oil of acid character, sweet, ester-like odor, heavier than water, sparingly soluble in water, easily soluble in alcohol, ether, etc. It decomposes and carbonizes upon distillation and cannot be solidified by a mixture of ice and salt. It is slowly soluble in concentrated aqueous solutions of sodium and potassium hydroxides, readily soluble in their alcoholic solutions, each solution having an *intense red color*.

Those who, in investigating petroleum, have had occasion to boil their distillates with nitric acid, have noticed upon shaking up these oils with alkalies, after the acid treatment, an intense red coloration. This property of dinitrohexane of turning red with alkalies, characteristic also of dinitroheptane and dinitrooctane, explains this fact, the cause of which was hitherto unknown. The higher primary dinitro-hydrocarbons seem in this respect to resemble the nitrolic acids.

Heptane, C_7H_{14}.

Normal heptane (boiling-point 98°–99°), specific gravity 0.7050 at 15°, behaves toward nitric acid much the same as hexane, but is capable of more rapid nitration, and of nitration by acid of somewhat greater dilution than in the case of hexane.

Nitric acid, of specific gravity 1.42, has been used for the preparation of the mononitro-derivative, the method of nitrating and of separating the products being exactly the same as that described for hexane.

The action of mixed sulphuric and nitric acids yields a considerable amount of dinitroheptane as a middle layer in the nitration flask, and this is easily obtained pure by mechanical separation, washing, and drying of this layer.

As has been stated before, the conditions are not favorable for quantitative comparisons of the rapidity of nitration. But the action of nitric acid, of specific gravity 1.42, gives with heptane as large a yield of nitro-products as is obtained from hexane in the same length of time by the action of fuming nitric acid—that is, about 20 per cent. of the theoretical yield by twenty hours' treatment. And, whereas the formation of dinitrohexane is difficult and the yield small, even by mixed sulphuric and fuming nitric acids, the formation of dinitroheptane is rather easy.

In the case of heptane, as in that of hexane, the hydrocarbon has been completely converted into nitro- and oxidation-products with a yield of perhaps 60 per cent. of crude nitro-compounds. No data have as yet been obtained relative to the time required for this complete conversion, but it does not take as much time as hexane.

Nitroheptane, $C_7H_{15}NO_2$.

The distillates for nitroheptane, collected chiefly at 193°–196°. This distillate, after washing and drying, gave on analysis the following results :

By Dumas' method 0.2242 gram oil gave 20.6 cc. nitrogen at 747 mm. and 18°.

	Calculated for $C_7H_{15}NO_2$.	Found.
N	9.70	10.11

Structure of Nitroheptane.—This nitroheptane gave, with potassium hydroxide, potassium nitrite, and sulphuric acid, the nitrolic-acid test, showing it to be *primary*.

About 3 grams was reduced to the amine by iron filings and dilute acetic acid, the reaction proceeding rapidly. The contents of the flask were then made alkaline with caustic soda and the liberated amine distilled off with steam. Carbon disulphide, alcohol, and mercuric chloride gave, with this amine, the mustard-oil reaction, and chloroform, alcohol, and caustic potash the isonitrile reaction, showing the amine to be *primary*.

The chlorplatinate was formed. Analysis of this compound showed it to be impure.

0.0456 gram substance gave, on ignition, 0.0155 gram platinum.

	Calculated for $(C_7H_{15}NH_2Cl)_2PtCl_4$.	Found.
Pt	29.82	33.98

It was noticed that too vigorous reduction of these nitroparaffins resulted in partial decomposition and the formation of some ammonia, gentle reduction giving the amines. It is probable that some ammonium chlorplatinate was contained in the compound analyzed, thus accounting for the high percentage of platinum.

Properties of Nitroheptane.—Nitroheptane, in all its properties so far observed, resembles nitrohexane very closely. It could not be solidified by ice and salt, and could be distilled without decomposition. It has much the same peculiar, ester-like odor as nitrohexane, and its solubility is the same.

Dinitroheptane, $C_7H_{14}(NO_2)_2$.

This compound, separated and purified in the same way as dinitrohexane, gave the following analytical results:

By Dumas' method, 0.1421 gram substance gave 18.4 cc. nitrogen at 738 mm. and 20° C.

	Calculated for $C_7H_{14}N_2O_4$.	Found.
N	14.74	14.37

Structure of Dinitroheptane.—As a dinitroparaffin, dinitroheptane should, on reduction, yield heptoic acid, hydroxylamine, and ammonia, according to the well-known reaction of this class of compounds,

$$RCH(NO_2)_2 + 8H = RCHO + 2H_2NOH + H_2O,$$
$$RCHO + NH_2OH = RCOOH + NH_3,$$

and this has been found to be the case.

About 5 grams of the dinitroheptane was reduced by means of tin and hydrochloric acid. The solution was diluted with water to about a liter, and then distilled in steam. The distillate thus obtained contained a very small quantity of a fatty acid, mixed with a small quantity of some neutral compound, probably an aldehyde. This fatty acid gave a characteristic insoluble copper salt but there was not sufficient for a quantitative determination. The solution left in the distilling-flask reduced Fehling's solution, showing the presence of hydroxylamine. This solution was then made alkaline with sodium hydroxide and distilled in steam, the odor of ammonia being apparent in the distillate. This distillate was evaporated to a small volume after acidifying with hydrochloric acid, and the double platinum salt formed. Analysis of this salt gave the following results:

0.3735 gram substance gave, on ignition, 0.1617 gram of platinum.

	Calculated for $(NH_4Cl)_2PtCl_4$.	Found.
Pt	43.92	43.30

Another attempt was made to obtain the heptoic acid by reducing about 5 grams of the dinitroheptane with tin and hydrochloric acid, diluting to about a liter, and extracting with ether. The ether was distilled off, the residue diluted with about a liter of water, and boiled with an excess of silver carbonate. The filtrate deposited, on evaporation and cooling, a very few crystals, but not sufficient for a determination of silver. But the formation of the hydroxylamine and ammonia indicates that the dinitroheptane is primary, represented by the formula $CH_3(CH_2)_5CH(NO_2)_2$.

Properties of Dinitroheptane.—Dinitroheptane is a clear, yellow oil, resembling dinitrohexane, but is less soluble in water than the latter. It has a similar, ester-like odor, and could not be solidified by a freezing-mixture of ice and salt. It decomposes by distillation and turns deep-red with alkalies.

Octane, C_8H_{18}.

Normal octane (boiling-point 124°–125°, specific gravity 0.7260 at 15°), when gently boiled with fuming nitric acid, of specific gravity 1.52, is acted upon violently, and much oxidation of the hydrocarbon results. Nitric acid, of specific gravity 1.42, and mixed sulphuric and nitric acids, react readily, without much oxidation of the hydrocarbon. Acid of greater dilution, even that consisting of one part nitric acid to four parts water, also acts upon the hydrocarbon, the action of course becoming slower the greater the dilution of the acid employed, but with the formation of the same products in every case, and the hydrocarbon is finally completely converted into nitro- and oxidation-products.

For the preparation of mononitrooctane, nitric acid of specific gravity 1.42 gives the best results, the action of the mixed acids resulting, as in the case of heptane, in the formation of considerable quantities of the dinitro-hydrocarbon. By employing either the 1.42 acid alone or the mixed acids, complete conversion of the hydrocarbon into nitro- and oxidation-products has been obtained in *eighteen to twenty hours*, with a yield of 60 or 70 per cent. of the theoretical quantity of nitrocompounds.

For the separation of the products the same method was employed as for those of hexane and heptane. In fractioning the mononitrooctane the same decomposition was noted upon first distillation as in the case of hexane and heptane, and this also has been found to be due to the dinitro-hydrocarbon.

Nitrooctane, $C_8H_{17}NO_2$.

The fractions for nitrooctane collected chiefly at 205°–210°, with some decomposition. A nitrogen determination in this fraction gave the following result:

By Dumas' method, 0.3938 gram substance gave 32.4 cc. (moist) nitrogen at 742 mm. and 22° C.

	Calculated for $C_8H_{17}NO_2$.	Found.
N	8.83	8.86

Structure of Nitrooctane. — With potassium hydroxide, potassium nitrite, and sulphuric acid, nitrooctane gave the nitrolic-acid test, characterizing it as *primary*.

About 5 grams was reduced to the amine by iron filings and acetic acid, the solution made alkaline with sodium hydroxide, and distilled in steam. The liberated amine gave both the isonitrile and the mustard-oil reaction, proving it to be primary.

Analysis of the double salt of platinum chloride and the octylamine gave the following figures:

0.1167 gram gave, on ignition, 0.0342 gram platinum.

	Calculated for $(C_8H_{17}NH_3Cl)_2PtCl_4$.	Found.
Pt	29.20	29.32

Still further evidence that the nitrooctane is primary, is afforded by the fact that it agrees in every respect with the primary nitrooctane made by Eichler[1] from octyl iodide and silver nitrite. It is a light-yellow liquid of ester-like odor, partially decomposing upon distillation, and resembling nitrohexane and nitroheptane in its solubility and other properties.

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[1] Ber. d. chem. Ges., **12**, 1883.

Dinitrooctane, $C_8H_{16}(NO_2)_2$.

Dinitrooctane was obtained by the action of mixed sulphuric and nitric acids upon octane, as a middle layer in the nitration-flask. After washing and drying, analysis gave the following results:

By Dumas' method, 0.3964 gram substance gave 46.0 cc. nitrogen at 750 mm. and 15° C.

By combustion, 0.4884 gram substance gave 0.8469 gram CO_2, and 0.3559 gram H_2O.

	Calculated.	Found.
C_8	47.06	47.27
H_{16}	7.84	8.08
N_2	13.73	13.63
O_4	31.37	31.02

Structure of Dinitrooctane.—To determine the structure of dinitrooctane it was reduced with tin and hydrochloric acid. If primary, octoic acid, hydroxylamine, and ammonia should be the products, and this was found to be the case.

About 5 grams of the oil were reduced with tin and hydrochloric acid, diluted with water to about 1 liter, and distilled in steam. A considerable amount of the fatty acid distilled with the steam. The silver salt of this acid was formed and analyzed.

0.1360 gram substance gave 0.0785 gram AgCl.

	Calculated for $C_7H_{15}COOAg$.	Found.
Ag	43.01	43.38

The residue in the distilling-flask reduced Fehling's solution rapidly, showing presence of hydroxylamine. This residue was made alkaline with sodium hydroxide and distilled in steam. The distillate, smelling strongly of ammonia, was acidified with hydrochloric acid, and the chlorplatinate formed. Analysis of the latter gave the following figures:

I. 0.2807 gram substance gave, on ignition, 0.1222 gram platinum.

II. 0.4885 gram substance gave, on ignition, 0.2137 gram platinum.

	Calculated for $(NH_4Cl)_2PtCl_4$.	Found.	
		I.	II.
Pt	43.92	43.54	43.75

Hence the dinitrooctane is primary, and is represented by the formula $CH_3(CH_2)_6CH(NO_2)_2$.

Properties of Dinitrooctane. Dinitrooctane is a clear, yellow oil of peculiar odor, somewhat heavier than water; it cannot be solidified by a mixture of ice and salt. It is turned intensely red by alkalies and resembles dinitrohexane and dinitroheptane in all of its observed properties.

Oxidation-products.

As mentioned before, the action of nitric acid upon these hydrocarbons is one of oxidation as well as of nitration. For the study of the oxidation-products, the hydrocarbon remaining after several nitrations was employed in each case, in order to preclude, as far as may be, the possibility of the presence of hydrocarbons other than the paraffins. This hydrocarbon was again treated with nitric acid of the desired concentration until the acid was exhausted, the spent acid neutralized with sodium carbonate, evaporated to dryness, and the salts examined.

The results of many experiments with hexane, with heptane, and with octane, with the employment of various concentrations of acid, has been to show that the same oxidation-products result from each hydrocarbon and from each concentration of acid. The work of Schorlemmer[1] and of Beilstein and Kurbatow[2] had indicated the probability of this result.

These oxidation-products are:

1. *Carbonic Acid.*—Determined in the escaping gases of the nitration-flask by its precipitation of solutions of calcium and barium hydroxides.
2. *Acetic Acid.*—Detected in the salts from the spent acid by its ethyl ester and its behavior with ferric chloride.
3. *Succinic Acid.*—Determined by precipitation with ammoniacal barium chloride and with ferric chloride in the cold.
4. *Oxalic Acid.*—Determined by the properties of its calcium and silver salts.

The formation of the first three products has been noted before by other investigators. Schorlemmer,[3] however, stated that no oxalic acid was formed by the oxidation of hexane, octane, or diamyl by nitric acid. Although numerous qualitative tests seemed to show that oxalic acid was present in each case, a quantitative determination was made for the purpose of furnishing definite proof.

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[1] *Loc. cit.*

[2] *Loc. cit.*

[3] *Loc. cit.*

The salts obtained by oxidation of heptane with 1.35 nitric acid for sixteen hours were dissolved in water, the succinic acid removed by boiling with ferric chloride and excess of sodium acetate, and oxalic acid precipitated in the filtrate by calcium acetate. The precipitate was filtered, washed, and dried, and the calcium determined.

0.0480 gram substance gave, on ignition, 0.0247 gram CaO, and this gave 0.0511 gram $CaSO_4$.

	Calculated for CaC_2O_4.	Found.
Ca	31.25	31.45

This proves the presence of oxalic acid. A blank experiment showed the reagents to be free from oxalic acid. The total amount formed in this case by boiling 97 grams heptane with 1.35 nitric acid for sixteen hours was only 0.04 per cent.

Carbonic acid is by far the most abundant oxidation-product. The quantity of the other oxidation-products formed by two days' boiling of the hydrocarbons with nitric acid, does not exceed 2 per cent.

These results seem to me to prove conclusively that the paraffins are rather readily capable of direct nitration. No trace of secondary or of tertiary nitro-compounds has been observed in these products, and this seems noteworthy, showing as it does that while, according to Konowalow, the normal paraffins give *only secondary* nitro-hydrocarbons when nitrated in sealed tubes, *only the primary* nitroparaffins are formed by nitration in an open vessel.

The dinitro-hydrocarbons are most probably formed by further nitration of the mononitro-hydrocarbons, and it is possible that the oxidation-products noted may be due to further action of the acid on one or both of these nitro-compounds. This will be investigated.

As this appears to be the first instance of the formation of primary nitroparaffins by direct nitration, and as only a very few of these higher nitroparaffins have ever been prepared in any way, the investigation is being continued. At present, experiments are in progress upon the nitration of the normal paraffins, hexane, heptane, octane, and nonane, with a study of the nature and properties of the nitro- and oxidation-products. The investigation will be extended so as to include other normal and isohydrocarbons, and an endeavor will be made to obtain data relative to the speed of the reaction and to the yield.

LAFAYETTE, IND., Jan., 1898.

Contributions from the Sheffield Laboratory of Yale University.

ON THE SILVER SALT OF 4-NITRO-2-AMINOBENZOIC ACID AND ITS BEHAVIOR WITH ALKYL AND ACYL HALIDES.

BY H. L. WHEELER AND BAYARD BARNES.

It is well known, from the work of Griess,[1] Lauth,[2] Michler,[3] Michael,[4] and others, that the alkali salts of the aminobenzoic acids do not give esters directly with alkyl halides, but that the alkyl groups attach themselves entirely or partially to nitrogen. In this respect the sodium salts of the acyl amides and those of the aminobenzoic acids are analogous.

The silver salts of the amides, however, behave differently;[5] here a replacement of the metal takes place and oxygen esters result, while the formation of nitrogen derivatives in this case has not been observed.

The action of alkyl and acyl halides on the silver salts of the aminobenzoic acids has, apparently, not been investigated, and it was with the object of investigating this action that the present work was undertaken. It seemed of interest to determine whether these silver salts behave like the silver salts of the amides and anilides or whether, like the sodium compounds, the entering groups attach themselves to nitrogen.

The new 4-nitro-2-aminobenzoic acid was selected as its esters are solids. We have found that the silver salt of this acid gives—as the chief product—with ethyl iodide in molecu-

[1] Ber. d. chem. Ges., **5**, 1038.

[2] Bull. Soc. Chim. (Paris), [3], **9**, 970.

[3] Ber. d. chem. Ges., **9**, 401.

[4] This JOURNAL, **7**, 198.

[5] Comstock and Kleeburg: This JOURNAL, **12**, 493, and **13**, 514; Tafel and Enoch: Ber. d. chem. Ges., **23**, 104 and 1554.

lar proportions, 4-nitro-2-ethylaminobenzoic acid; the ethyl group attaching itself to nitrogen, and, next, in smaller quantity, 4-nitro-2-ethylaminoethyl benzoate is formed, while no 4-nitro-2-aminoethyl benzoate was observed.

The behavior of the silver salt with ethyl iodide is therefore analogous to that of the above-mentioned sodium compounds. In this connection it may be remarked that Kraut[1] found that the silver salt of aminoacetic acid does not give the simple ester with ethyl iodide, when these compounds are used in molecular proportions, but the triethyl derivative of the ester and in the same manner betaïn methyl ester results.

On the other hand Curtius[2] found that the methyl and ethyl esters of acetyl glycin result from the silver salt, therefore the metal in this salt is directly replaceable. We have found, precisely in accordance with this, that if 4-nitro-2-aminobenzoic acid is acetylated, then both the sodium and silver salts give oxygen derivatives.

The action of acyl chlorides on the silver salt of anthranilic acid and on 4-nitro-2-aminobenzoic acid might lead to the formation of mixed anhydrides analogous to the action of acetyl chloride on sodium benzoate.[3] We have found, however, that in the presence of the amino group the acyl group attaches itself entirely to nitrogen. A similar result was observed in the case of aminoacetic acid by Kraut,[4] Hartmann,[5] and Curtius.[6] They prepared acetylaminoacetic acid from the silver salt of glycin and acetyl chloride, and Curtius showed that hippuric acid is thus formed. The silver salts of the anilides also give nitrogen derivatives with acyl halides.[7]

The sodium salts of the amides were formerly universally represented as having the metal attached to nitrogen, since they give nitrogen alkyl compounds with alkyl halides. As shown here, the silver salt of the aminobenzoic acids, which contain the metal joined to oxygen, nevertheless, give nitrogen derivatives with ethyl iodide, etc., and silver is generally more readily replaceable than sodium. It is shown from this, as has frequently been suggested, that the position of the metal in the salts of the amides cannot be determined by the structure of the reaction product, and that the sodium salts of the amides may leave the metal joined to oxygen. If now, with this view, we arrange the salts of the amino and acetamino acids with those of the amide, according to their behavior with alkyl halides, we have the following :

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[1] Ann. Chem. (Liebig), **182**, 172.

[2] Ber. d. chem. Ges., **17**, 1672.

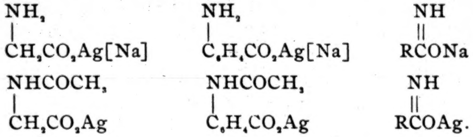
[3] Gerhardt: Ann. Chem. (Liebig), **87**, 81.

[4] *Loc. cit.*

[5] Ann. Chem. (Liebig), **133**, 105.

[6] J. prakt. Chem. [2], **26**, 170.

[7] Wheeler and Boltwood: This JOURNAL, **18**, 381.



$$\begin{array}{llll} & NH_2 & NH_2 & NH \\ \text{I.} & | & | & \| \\ & CH_2CO_2Ag[Na] & C_6H_4CO_2Ag[Na] & RCONa \\ & NHCOCH_3 & NHCOCH_3 & NH \\ \text{II.} & | & | & \| \\ & CH_2CO_2Ag & C_6H_4CO_2Ag & RCOAg. \end{array}$$

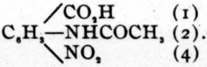
The fact that the first series give nitrogen derivatives is explained by the positive character of the amido and imido groups ; here the alkyl halide reacts by addition to the nitrogen, there being a subsequent separation of hydrogen halide, or, in the case of the amides, of sodium halide.

In the second series either these groups or the molecules are more negative and additions to the nitrogen do not take place, but instead the metal is replaced by alkyl.

The above affords further data for and confirms the conclusion of Nef, Hantzsch,[1] Freer and Sherman,[2] and others, that the sodium in the salts of the amides and anilides is joined to oxygen. The amides and anilides, in general, have the normal structure, while the salts, with the possible exception of the mercury compounds, are derivatives of the pseudoform and contain the imido group. It is certain that most if not all the reactions of these compounds involve, as the first step, addition. These unstable addition-products then decompose into more stable derivatives, which latter constitute the products that are isolated.

Experimental Part.

4-Nitro-2-acetaminobenzoic Acid,



$$C_6H_3\begin{cases} CO_2H & (1) \\ NHCOCH_3 & (2) \\ NO_2 & (4) \end{cases}.\text{—}$$

This acid was prepared by oxidizing 4-nitro-2-acettoluide with a 1 per cent. solution of potassium permanganate. The operation being essentially the same as that employed by

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[1] Ann. Chem. (Liebig), 296, 91.

[2] This JOURNAL, 18, 570.

Bedson[1] in oxidizing orthoacettoluide. Bedson obtained a yield of only 32 per cent. of acetylorthoaminobenzoic acid. Apparently the nitroacettoluide is oxidized more smoothly since we have obtained yields varying from 44 to 77 per cent. of the calculated. The best yield is obtained when the quantity of toluide employed does not exceed 50 grams. On filtering, concentrating, and acidifying the solution after oxidizing, the acid separates as a yellowish-white precipitate. It crystallizes from alcohol in long, light yellow needles, which melt at about 215°. A nitrogen determination gave :

	Calculated for $C_9H_8N_2O_5$.	Found.
N	12.5	12.4

It was observed that acids saponify this acetyl compound more readily than alkali.

The sodium salt was obtained as a bright yellow precipitate by adding one molecule of sodium ethylate to an absolute alcohol solution of the acid. It is readily soluble in water and somewhat in alcohol.

The silver salt is precipitated in a bright yellow, gelatinous form when silver nitrate is added to an aqueous solution of the sodium salt. It was found best to make the precipitation at a temperature of about 70°, then, on stirring vigorously, the precipitate becomes granular and is more readily filtered. It can be dried at 100° and is quite stable when exposed to light.

	Calculated for	Found.	
	$C_9H_7N_2O_5Ag$.	I.	II.
Ag	32.6	32.35	32.31

Ethyl 4-nitro-2-acetaminobenzoate was prepared by heating the above sodium salt with an excess of ethyl iodide in a sealed tube at about 190° for eight hours. The product was extracted with water and then crystallized from alcohol and finally from ligroïn, when it melted at 112°. It forms bright yellow plates or flattened prisms. This compound is more readily formed, however, from the silver salt. A nitrogen determination in a product thus obtained gave :

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[1] Jour. Chem. Soc., 1880, 752.

	Calculated for $C_{11}H_{12}N_2O_5$.	Found.
N	11.11	10.77

When this compound is treated with cold sodium hydroxide the ethyl group is removed, leaving the acetyl group unaffected; on the other hand, when it is warmed with sulphuric acid, in alcoholic solution, the acetyl group alone is removed.

4-Nitro-2-aminobenzoic Acid.—This was best obtained by warming the acetyl compound in alcohol with acids. It separates from alcohol in long, bright-red needles. On heating it begins to darken at 260°, and then melts with decomposition at 264°. A nitrogen determination gave:

	Calculated for $C_7H_6N_2O_4$.	Found.
N	15.38	15.29

The ammonium salt was formed when dry ammonia gas was passed into an ethereal solution of the acid. It dissolves readily in water.

	Calculated for $C_7H_9N_3O_4$.	Found.
NH_3	8.58	8.49

The sodium salt was obtained as a bright-red precipitate when one molecular proportion of sodium ethylate was added to the alcoholic solution of the acid. It is quite soluble in water and sparingly in alcohol.

The silver salt was obtained as a pink, gelatinous precipitate when the above sodium salt was dissolved in water and the requisite amount of silver nitrate was added. On warming to about 50° and stirring, it coagulates to a tan-colored powder. The yield corresponds to the calculated.

	Calculated for $C_7H_5N_2O_4Ag$.	Found.
Ag	37.37	37.30

On treating this salt, suspended in ether, with the calculated quantity of acetyl chloride, enough heat was liberated to cause the solution to boil. It was warmed until the odor of acetyl chloride disappeared, then filtered, and evaporated over potassium hydrate in a vacuum desiccator. The crystals that separated proved to be 4-nitro-2-acetaminobenzoic acid.

Methyl 4-nitro-2-aminobenzoate, obtained by boiling the acid with methyl alcohol and sulphuric acid, melts at 157°. It is soluble in ligroïn and alcohol and separates in dark, orange-colored clusters of needles.

	Calculated for $C_8H_8N_2O_4$.	Found.
N	14.28	14.15

Ethyl 4-nitro-2-aminobenzoate was obtained by boiling the acid with alcohol and hydrogen chloride. It forms dark, orange-colored plates, which are quite soluble in alcohol and benzene.

	Calculated for $C_9H_{10}N_2O_4$.	Found.
N	13.33	13.38

4-Nitro-2-ethylaminobenzoic Acid.—This was the chief product formed when the silver salt of the amino acid was suspended in ether and warmed with the calculated quantity of ethyl iodide for three days, the reaction then being practically complete. The ethereal solution was evaporated and the residue treated with dilute sodium hydroxide; on filtering and acidifying the alkaline solution, this compound separated as a bright yellow precipitate. On crystallizing from alcohol and benzene it separated in the form of golden-yellow plates, which melt at about 223°. A nitrogen determination gave:

	Calculated for $C_9H_{10}N_2O_4$.	Found.
N	13.33	13.48

Ethyl 4-nitro-2-ethylaminobenzoate.—The part insoluble after the above treatment with alkali proved to be this diethyl derivative. It is formed in smaller quantity than the nitrogen monoethyl derivative. From benzene and alcohol, in which it is very soluble, it separates in the form of long, pale-yellow needles; these melt at 80°.

This compound was also formed when 4-nitro-2-ethylaminobenzoic acid was boiled with alcohol and sulphuric acid; an analysis therefore seemed superfluous.

Acetylorthoaminobenzoic acid was obtained when the silver salt of anthranilic acid was treated with acetyl chloride. It forms white prisms melting at 185°, as observed by Döbner and Miller.[1]

NEW HAVEN, CONN.,
January, 1898.

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[1] Ber. d. chem. Ges., **15**, 3077.

Contribution from the Laboratory of General Chemistry, University of Michigan.

FORMAMIDE AND ITS SODIUM AND SILVER SALTS.

By Paul C. Freer and P. L. Sherman, Jr.

In continuing our work on the various derivatives of formic acid with a view to determining the constitution of the formyl group, it was found necessary to use pure formamide. The various methods for its preparation were therefore carefully tried. A. W. Hofmann,[1] Behrend,[2] Lorin,[3] and Basarow[4] have all contributed methods, the details of which are more or less carefully described. The latter two methods need not be commented upon here, as no attempt was made to secure pure formamide. Hofmann digested dry ethyl formate with dry ammonia and heated the product in sealed tubes for two days, at 100°. The ammonium formate formed was then distilled. Behrend first heated ammonium formate with urea, and then distilled the product in a partial vacuum. The analyses given are as follows:

	Hofmann.	Behrend.	Calculated for $HCONH_2$.	Calculated for $HCOOH$.	Calculated for NH_4CN.	Calculated for $HCOONH$.
C	27.61	26.43	26.67	26.08	27.27	19.04
H	6.71	6.89	6.67	4.34	9.09	7.93
N	....	30.87	31.11	....	63.63	22.22

In order to see if these analyses denoted pure products, the distillation of both ammonium formate and pure formamide at ordinary pressure and in a partial vacuum was carefully studied and the following results noted:

When ammonium formate is heated in a distilling-flask, water and ammonia begin to distil at about 100°, both products continuing to increase as the temperature slowly rises. At 150° the distilling liquid contains noticeable amounts of formic acid, and these continue to increase up to the temperature of about 185°–190°, when formamide begins to pass over, and from this time on forms the leading product.

Between 180°–200°, however, three side reactions occur, which not only lower the yield of formamide but render it impossible to make pure formamide according to this method.

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[1] Jour. Chem. Soc. [2], 1-72.

[2] Ann. Chem. (Liebig), **128**, 335.

[3] Compt. rend., **59**, 51.

[4] Ber. d. chem. Ges., **4**, 409.

The first reaction referred to is the dissociation of the ammonium formate, which is still undecomposed in the distilling-flask, into formic acid and ammonia. The ammonia is given off as a gas and the formic acid distils over. If care is taken to provide the flask with a long water condenser, the formic acid will, to a large part, unite with the ammonia while on the way to the receiver, often in such quantities as entirely to stop the tube of the condenser. When only an air condenser is used, the tube soon becomes hot enough to prevent the crystallization of the ammonium formate, and it passes into the receiver as a thick, colorless liquid, not to be distinguished from the formamide which distils at the same time.

Besides this dissociation of the ammonium formate, which seems to have been overlooked, there is a second side reaction, noticed by Hofmann, according to which formamide decomposes into carbon monoxide and ammonia while undergoing distillation. The third side reaction is the decomposition of formamide into prussic acid and water. This latter reaction takes place mostly after the temperature of the distilling vapors has reached 195°. The prussic acid unites to some extent, as did the formic acid, with the ever-present ammonia and is found in the distillate as ammonium cyanide; the water unites with the formamide in the receiver to form ammonium formate.

The products of distillation of ammonium formate under ordinary pressure are, therefore, water, ammonia, formic acid, formamide, ammonium formate, carbon monoxide, prussic acid, and ammonium cyanide. These products taken together give the distillate an acid reaction, and vary decidedly in their proportions according to the rate of distillation, the kind of condenser used, and the amount of ammonium formate distilled. Even in fractions having an almost constant boiling-point, the presence of two or more of the above-mentioned products could be easily proved. Analyses of these fractions gave percentages for carbon, hydrogen, and nitrogen agreeing well with those for formamide. The reason for this, however, is seen by a study of the percentages calculated for formic acid, ammonium formate, and ammonium cyanide, and given in the table above.

The attempt was then made to purify the distillate by distillation in a vacuum. It was found that while the decomposition of formamide was prevented to a larger extent, the dissociation of the ammonium formate took place more readily than at ordinary pressure, and at a temperature so nearly that at which the formamide distilled, that no separation could be effected in this way.

In order to insure the complete decomposition of ammonium formate into water and formamide, and at the same time to prevent the dissociation of ammonium formate and the decomposition of formamide, the following process was tried with good results: Pure formic acid was neutralized with concentrated ammonia, and the half-solid mass poured into a distilling-flask, and heated about two hours at a temperature beginning at 100° and increasing gradually to 180°. The dissociation of the ammonium formate was prevented by means of dry ammonia gas, which was run in constantly until the decomposition was complete and no more water distilled over even at a temperature of 180°. The ammonia was dried over stick alkali and metallic sodium wire, and acted as a dehydrating agent while it prevented effectually the dissociation of the ammonium formate. When the current of ammonia was stopped, even momentarily, the dissociation of the ammonium formate began at once. The vapors of formic acid filled the distilling-flask and began to distil over. With the introduction of new ammonia gas the formic acid was neutralized, and the ammonium formate was deposited in feathery crystals on the cool sides of the flask and condenser.

When the decomposition of the ammonium formate was complete, the resulting amber-colored, heavy, oily liquid was cooled in the current of ammonia, and then fractioned in an atmosphere of ammonia under a pressure of about one-half mm., which insured the minimum amount of decomposition. A large U-tube, filled with pumice stone and concentrated sulphuric acid, was introduced between the receiver and the pump, and after the excess of ammonia had passed over, no more gas was observed to pass through the sulphuric acid. The first portions of the distillate were discarded, to be worked up again. The rest of the distillate, which boiled at 85°–95°,[1] was perfectly colorless, oily, possessed a high index of refraction, reacted neutral towards litmus, and when kept well stoppered, as it is very hygroscopic, did not decompose, even after months of summer weather.

At —1° it solidifies to a white crystalline mass of long, irregular needles. When even small quantities of ammonium formate are present, or any other impurity, in fact, the melting-point of formamide is very much lowered.

The specific weight of formamide, taken at 4°, was found to be 1.16. The specific weight for acetamide is given by Mendius as 1.12,[2] and for propionamide, by Schroeder,[3] as 1.03.

Formamide dissolves in water in all proportions without decomposition at first; even dilute alkali does not decompose it at 0°. At room temperature it gives off ammonia at once.

When distilled at ordinary pressure, it begins to decompose at 100°, giving off ammonia, carbon monoxide, prussic acid, and water. No liquid distillate passes over under 200°, the first that appears being dark amber in color, which darkens on standing. The rest of the distillate was colorless at first, but gradually darkened. The entire product distilled between 203°–216°. In the distillate water, ammonia, and prussic acid were found. Crystals of ammonium formate were seen at the beginning of the distillation on the sides of the condenser.

Sodium Formamide.—This compound was prepared as previously described,[4] pure formamide being used in its formation. It was found to be quite stable when pure, although decomposing at once under the influence of either heat or moisture. Organic halogen compounds, such as ethyl iodide, acetyl chloride, or benzoyl chloride, could not be made to react with it.

Dissolved in absolute alcohol, it gives a pure white, curdy precipitate when brought in contact with alcoholic silver nitrate. This silver compound is very sensitive to both light and heat, and darkens quickly, depositing a mirror of metallic silver.

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[1] The boiling-point under this pressure, can be given only approximately, as almost imperceptible changes in the pressure made large variations in the boiling-point.

[2] Beilstein [III], 1, 1236.

[3] Ber. d. chem. Ges., 12, 562.

[4] This JOURNAL, 18, 580.

Titherly,[1] in his work on sodamide, prepared the sodium salts of several acid amides in a new way, by allowing sodamide to react on the acid amide while suspended in boiling benzene, until the evolution of ammonia ceased. The sodium salts thus prepared were white crystalline powders, and in other ways corroborated the work already done on these bodies.[2] The yield, in every case given, was described as being theoretical, though no method for removing the excess of either the sodamide or the acid amide was given.

However, when these sodium salts were dissolved in absolute alcohol and treated with alcoholic silver nitrate, they all gave brightly colored precipitates; with formamide, orange-red; with acetamide, bright orange-red; with propionamide, orange; and with benzamide, orange-brown. Titherly sought to explain the difference in the color between the silver salts prepared by himself and those prepared by others[3] by assigning to his the constitution R—CO—NHAg, and to the other the constitution R—C(OAg)=NH. In view of the fact, however, that we prepared a white silver formamide in exactly the same manner as Titherly prepared his colored salt, it might be supposed that there were two kinds of sodium salts of the acid amides before us.

To disprove the correctness of this assumption we prepared sodium formamide according to the method given by Titherly.[4] The theoretical quantities of sodamide and formamide, the latter being in slight excess, were suspended in dry benzene and boiled for two hours. A small part of the white powder, which had precipitated, was taken out, dissolved in absolute alcohol, and added to alcoholic silver nitrate. The precipitate which formed was bright orange in color. After another hour's steady boiling, however, the reaction-product gave a pure white precipitate with silver nitrate, which quickly blackened on exposure to light and heat, and was therefore identical with the silver formamide prepared by us. As sodamide, even in very dilute solutions, gives a bright-orange precipitate with silver nitrate, it is probable that this substance was present in the sodium formamide at the time it was tested by Titherly, and hence caused the colored precipitate, rather than that the longer heating changed the sodium salt first formed into its desmotropic form.

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[1] Jour. Chem. Soc., **73**, 460.

[2] Titherly describes sodium formamide as if it were a new substance. He apparently overlooked our work of the previous year. See also Curtius: Ber. d. chem. Ges., **23**, 3039: Blacher: *Ibid*, **28**, 432 and 2352.

[3] Tafel and Enoch: Ber. d. chem. Ges., **23**, 104; Beilstein [III], **1**, 1237.

[4] Jour. Chem. Soc., **72**, 467.

As a further proof that unchanged sodamide was always present in those sodium salts which gave colored silver precipitates, sodium acetamide, prepared according to Titherly's directions, was decomposed with ice-water, to which some Nessler's reagent had been previously added. A yellow color, that appeared after a few moments, denoted the presence of ammonia, and hence indicated the decomposition of sodamide, while sodium acetamide, prepared according to Blacher, gave no test for ammonia even after an hour's standing.

The above experiments lead to the conclusion, therefore, that so far only one series of sodium and silver salts of the acid amides has been found, and that the silver compounds are all white, easily decomposable bodies.

Concerning the constitution of these bodies, as well as of the sodium compounds from which they were made, further evidence is necessary. From the experiments made by Blacher,[1] Comstock and Wheeler,[2] Tafel and Enoch,[3] and others,[4] they conclude that in the sodium amide bodies the sodium is attached directly to the nitrogen, while in the silver compounds, on the other hand, the silver is attached to oxygen. The reactions which they carried out with the higher aliphatic and the aromatic acid amides do not succeed with sodium and silver formamide. That the latter need not be assigned another constitution on this account, is evident, for this indifference in the reactivity of the sodium and silver atoms is probably due to the peculiar nature of the formyl group. The arguments of Titherly, based upon the different color of his silver compounds have, in view of the above work, no value.

ANN ARBOR, January, 1898.

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[1] Blacher: Ber. d. chem. Ges., **28**, 432, 2352.

[2] Comstock and Wheeler: This JOURNAL, **13**, 514.

[3] Enoch and Tafel: Ber. d. chem. Ges., **23**, 104.

[4] Wheeler and Walden: This JOURNAL, **19**, 129.

ON THE DECOMPOSITION OF DIAZO COMPOUNDS.

XIII.—A STUDY OF THE REACTION OF THE DIAZOPHENOLS AND OF THE SALTS OF CHLOR- AND BROMDIAZOBENZENE WITH ETHYL AND WITH METHYL ALCOHOL.[1]

BY FRANK KENNETH CAMERON.

The special investigation, the results of which are here recorded, was on the influence of the hydroxyl group, and the elements chlorine and bromine, when substituted in the benzene nucleus, in determining the decomposition of diazo compounds with ethyl and methyl alcohols.

The decomposition of these compounds with water[2] has been studied ; it takes place normally, and it does not seem desirable, in this connection, to do more than refer to these investigations for the sake of completeness.

The Diazo Phenols.

Ample quantities of ortho- and paramidophenol hydrochlorates were at my disposal, and I was especially fortunate in having a kilogram of the free base, metamidophenol, available for this research.

Paradiazophenol chloride was prepared by the method of Schmidt.[3] The paramidophenol hydrochlorate was finely pulverized in an agate mortar, and then poured into a beaker containing a saturated solution of nitrous oxide in alcohol, and surrounded by a freezing-mixture of crushed ice and hydrochloric acid. The mixture was stirred for about five minutes, then allowed to settle for a few minutes, and carefully decanted, so as to leave any undissolved amido salt. The solution rapidly became dark-blue. On the addition of much ether, and strongly cooling, the diazo compound separated in fine white crystals, which were filtered off with the aid of a pump, and dried on bibulous paper. It soon decomposed in the air, gradually becoming a bright crimson in color. Heated on platinum foil, it decomposed, with formation of violet fumes, much resembling in appearance iodine vapor, and left no residue when freshly prepared.

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[1] From the author's thesis, submitted to the Board of University Studies of the Johns Hopkins University for the degree of Doctor of Philosophy, June, 1894. The work was undertaken at the suggestion of Professor Remsen and carried on under his guidance.

[2] Ber. d. chem. Ges., **1**, 67 ; **5**, 777 ; **7**, 905 ; **9**, 1160 ; **11**, 1161 ; **8**, 362 ; Ann. Chem. (Liebig), **176**, 30-45.

[3] Ber. d. chem. Ges., **1**, 68.

20 grams of the diazo compound, with 150 cc. ethyl alcohol, was placed in a flask fitted with an inverted condenser, and slowly warmed. Decomposition commenced at once, the solution becoming reddish-brown, a gas being given off, and a strong odor of aldehyde perceived. The decomposition appeared completed in about an hour. The alcohol was then distilled off, the residue distilled with steam, and the distillates examined. As nearly as I could determine, the hydrogen reaction alone took place. Undoubtedly, phenol was formed in considerable quantity, and was identified by precipitating with bromine water, recrystallizing the precipitate, tribromophenol, and determining its melting-point. There was no evidence of any other definite decomposition-product. A considerable tarry residue remained after the distillation. This was examined, and attempts made to extract something definite with ether, benzene, ligroïn, chloroform, glacial acetic acid, acetone, etc., but without success.

20 grams of the diazo compound was treated with 150 cc. methyl alcohol. Decomposition commenced on warming, but not so readily as in the last experiment, the diazo salt, in the earlier part of the experiment, crystallizing, to some extent, in beautiful, shell-like aggregates on the sides of the flask. The decomposition was completed in about one and one-half hours. After distilling with steam, the distillate was examined, phenol identified, but no other definite product could be isolated.

Weselsky and Schuler,[1] studying the action of water on paradiazophenol chloride, found the reaction was cleaner in the presence of a dilute acid.

Therefore, 20 grams of the diazo compound was treated with ethyl alcohol, containing 20 per cent. sulphuric acid. The decomposition was somewhat slower and cleaner. Phenol and aldehyde were the only products that could be identified.

20 grams of the diazo compound was then decomposed in

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[1] Ber. d. chem. Ges., 9, 1160.

ethyl alcohol, saturated with hydrochloric acid, a stream of the dry gas being constantly passed through the solution during the reaction. The decomposition required about five hours for completion, and was cleaner than in the last experiment. Phenol and aldehyde were the only products that could be identified.

20 grams of the diazo compound was decomposed in ethyl alcohol, containing 20 per cent. of caustic potash. Decomposition took place at once, and was very rapid, being completed in about twenty minutes. A very large quantity of a tarry material was produced. Nothing but phenol could be identified, which was isolated as potassium phenolate.

20 grams of the diazo compound was decomposed in ethyl alcohol saturated with ammonia, and a stream of the gas, previously dried by passing over coarsely powdered quicklime, was conducted through the solution during the reaction. The flask in which the decomposition took place, was kept surrounded with ice-water. The decomposition commenced at once, and proceeded evenly, being completed in about two hours. No definite product other than phenol could be isolated. The odor of aldehyde was distinctly noticed, and its presence proved with a hot ammoniacal solution of silver nitrate.

20 grams of the diazo compound was decomposed with methyl alcohol, in the presence of ammonia, as in the last experiment. After the completion of the reaction, the alcohol was distilled off and the residue distilled with steam. The presence of phenol in both distillates was proved. The water distillate, on standing, changed color to bright green, and finally to an intense, beautiful blue, which changed to a bright red on the addition of an acid, and was restored when an excess of alkali was added. The color changes were very sharp and extremely delicate. An experiment made to determine the point, indicated that this color-reaction was due to a dye-stuff, formed by the oxidation in alkaline solution, of the product of the reaction of phenol on amidophenol. The presence of the amidophenol was probably due to some of it dissolving in the alcohol, without being acted upon by the nitrous acid in the diazotizing process. This coloring-matter

was probably present in very small quantities, as it was shown to have intense coloring-power.

20 grams of the diazo compound was decomposed in methyl alcohol saturated with hydrochloric acid, a stream of the dry gas being constantly passed through during the reaction. The decomposition was slow and regular, it being necessary to boil for about eight hours for completion. Phenol was the only product that could be identified.

There are several recorded cases of the decomposition of diazo compounds in the presence of sulphur dioxide. In this way Hübner,[1] in certain cases, was able to prepare the corresponding sulphonic acid. This suggested the following experiment:

40 grams of the diazo compound was decomposed in methyl alcohol saturated with sulphur dioxide, and a stream of the dried gas was passed through the solution during the decomposition, which required about eight hours at the boiling-point of the alcohol for completion. The alcohol was distilled off and shown to contain phenol. The residue was then carefully dried over the water-bath to insure the elimination of any hydrochloric acid, and then boiled with water and barium carbonate. It was then filtered and the filtrate examined for barium, but none was present. It is therefore improbable that a sulphonic acid was formed. No other definite product could be isolated.

It now seemed desirable to try the effect of sulphur dioxide in some neutral medium, which does not itself react with the diazo compound.

Therefore, 20 grams of the diazo compound was suspended in anhydrous ether, and a stream of sulphur dioxide passed in until the ether became saturated. Except a slight alteration in the color of the diazo compound, probably caused by the air brought in contact with it in the early part of the experiment, there was no evidence of any reaction taking place.

20 grams of the diazo compound was suspended in anhydrous ether, the whole surrounded with ice-water, and a stream of dry ammonia passed in. Decomposition commenced at once, and was quickly completed, the mass becom-

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[1] Ber. d. chem. Ges., **10**, 1715.

ing black and tarry in appearance, but apparently containing some granular material. The ether was filtered off, the residue dried on bibulous paper, and examined. It apparently contained some amidophenol hydrochlorate, mixed with ammonium chloride, but it was not possible to separate them, and no definite statements can be made regarding the reaction.

Experiments were tried with the diazo compound and methyl alcohol, in which aniline or substituted anilines had been dissolved. In all these cases reaction took place at once, even in the cold, a gas being given off. Dilute acid was then added sufficient to dissolve out any unused aniline. The gummy residue was then filtered off, dried, and examined. No definite results, however, could be obtained.

Orthodiazophenol Chloride.—After a number of experiments I found that the best method, on the whole, for the preparation of the compound, was to make a thin paste of *o*-amidophenol hydrochlorate in alcohol, to keep this well cooled by a freezing-mixture, and to pass in rapidly a stream of nitrous acid, previously well cooled, until the whole mass was in solution, and the gas was no longer absorbed. The dark-colored solution resulting was then poured into a large quantity of well-cooled ether. The diazo salt soon separated out, but was generally slightly discolored greenish, which soon turned to brown on exposure to the air. A very pure specimen was obtained by dissolving in methyl alcohol at the room-temperature, and reprecipitating with strongly cooled ether. It soon became discolored on standing. Decomposed by heating on platinum foil, it gave off brownish fumes, and left a small residue of finely divided charcoal.

20 grams of the diazo compound was dissolved in ethyl alcohol, a marked diminution of temperature being noticed, and the solution becoming greenish in color. There was but little decomposition until the solution was warmed nearly to boiling, when it proceeded evenly and was completed in about three hours. Aldehyde was given off. The alcohol was distilled off and, on examination, was shown to contain phenol. The residue was now transferred to a distilling-bulb, and distilled, a mixture of alcohol and phenol distilling over until the

thermometer indicated 178°–180°, the boiling-point of phenol. After standing at this point for some time, it rapidly fell, a very small quantity of some crystalline material subliming from the residue at the same time. This sublimate could not be identified, and appeared to be a mixture.

20 grams of the diazo compound was dissolved in methyl alcohol, with marked lowering of the temperature. The decomposition was completed after boiling for about seven hours. The alcohol was distilled off and shown to contain phenol. The tarry residue was distilled, yielding phenol, but no other definite products.

50 grams of the diazo compound was decomposed in methyl alcohol saturated with hydrochloric acid, the decomposition being completed after boiling for about nine hours. The alcohol was distilled off and shown to contain phenol. The residue was distilled with steam, more phenol passed over, and a very small quantity of a yellow substance solidified in the condenser, which was shown by its melting-point and physical properties to be *o*-nitrophenol. Some of the original amido salt was then distilled with steam, and was found to contain a small quantity of unreduced *o*-nitrophenol.

40 grams of the diazo compound was then decomposed with methyl alcohol, in the presence of sulphur dioxide. The decomposition was completed after boiling for about nine hours. Attempts to detect the presence of a sulphonic acid were unavailing. Phenol was the only substance that could be identified.

Metadiazophenol Chloride.—The metamidophenol hydrochlorate was prepared as described by Ikuta,[1] with this modification, that it was crystallized from concentrated solutions by surrounding it with a freezing-mixture. After a number of attempts to prepare the diazo compound, and with very poor success, the following method was devised, and found to be quite satisfactory. The amido salt was dissolved in just sufficient 95 per cent. alcohol. A calculated amount of amyl nitrite was dissolved in about half the quantity of alcohol, and surrounded with a freezing-mixture of crushed ice and hydrochloric acid. Into this the solution of the amido salt was slowly poured, in very small quantities at a time, the whole being well stirred, and the temperature at no time allowed to rise to 0° C. After standing a few minutes, it was poured into a large amount of well-cooled ether. The diazo salt separated at once as a white crystalline precipitate, which soon changed color to red, and then brown. It was filtered rapidly with the aid of the pump, washed with dry ether, and dried as quickly as possible on a porous plate or bibulous paper, in as cool a place as was available. The freshly prepared compound was very unstable, exploding when struck or heated. 30 grams of the amido salt yielded 33 grams of the diazo salt.

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[1] This JOURNAL, **15**, 39.

A. Bantlin[1] treated a solution of metamidophenol in dilute sulphuric acid with potassium nitrite, and boiled with evolution of nitrogen. After cooling he extracted with ether, and obtained resorcinol from the extract. It seemed desirable to try the reaction with the diazo compound itself, however. Therefore, 30 grams of the diazo compound was dissolved in water and boiled. The decomposition was very rapid, a large amount of tarry material being formed. Extracted repeatedly with ether, and the extract evaporated, a dark-colored, disagreeable-looking residue was obtained, which, after standing several days, deposited white needles, but much discolored by a black tarry residue, from which it was impossible to separate them by crystallization. The yield was very small.

30 grams of the diazo compound was decomposed in water containing about 10 per cent. hydrochloric acid. The reaction appeared to be somewhat cleaner than in the last experiment. It was distilled with steam until the distillate no longer gave a precipitate with bromine water. Bromine water was now added until no further precipitate was obtained, the precipitate filtered off, recrystallized from alcohol, and identified by its melting-point as tribromresorcinol.

15 grams of the freshly prepared diazo compound was decomposed in ethyl alcohol. Decomposition commenced at once, and appeared to be complete in about an hour. It was then heated to boiling with apparently no further decomposition. The alcohol was distilled off and shown to contain phenol. Distilled with steam, more phenol came over and a tarry resi-

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[1] Ber. d. chem. Ges., 11, 2101.

due was left in the flask. This residue was extracted with benzene and chloroform without success. It was then distilled, yielding a small quantity of phenol, and then charring.

30 grams of the diazo compound was decomposed with methyl alcohol. The decomposition commenced at once, and was completed in about an hour and a half. The alcohol was distilled off and the residue distilled with steam. Phenol was proved present in both distillates. No other product could be isolated.

Preparation of the Chlordiazobenzene and Bromdiazobenzene Salts.

The chlordiazobenzene salts, and the bromdiazobenzene salts used in this investigation, were all prepared in the same manner, and one description will apply to them all if the names of the particular anilines and acids be interpolated.

A weighed amount of the aniline was dissolved in a slight excess of the acid, and sufficient water added to make a thick paste, when surrounded with a freezing-mixture.

A rapid stream of nitrogen trioxide, prepared by decomposing strong nitric acid with arsenic trioxide, was passed through the paste, until the whole dissolved to a clear, dark-green solution, and the gas was no longer absorbed. The diazo salt was then precipitated by adding to a strongly cooled mixture of alcohol and ether. It was filtered off with the aid of the pump, washed with dry ether, and then dried on an unglazed plate and bibulous paper.

These salts were all white, crystalline substances, fairly stable in the air, and in no case here recorded was a discolored or suspicious specimen used.

The decompositions were carried on in suitable flasks fitted with return condensers, and arranged over wire gauze, as this was found to be most convenient for controlling the temperature during a reaction.

o-Chlordiazobenzene Nitrate.—20 grams *o*-chloraniline yielded 18 grams of the diazo salt.

15 grams of the diazo compound was added to about 150 cc. ethyl alcohol. It partially dissolved without decomposition. Warmed until decomposition had fairly commenced, the lamp

was withdrawn, and it proceeded spontaneously, evenly, and regularly, and appeared to be complete in about an hour and a half. It was then boiled for a half hour, to insure complete decomposition. Aldehyde was given off copiously during the reaction. Distilled with steam an oil passed over, which, separated and dried over calcium chloride, weighed 7.6 grams. It was distilled, boiling at 132°, and was identified as chlorbenzene. A small residue of tarry material was carefully examined, but from it nothing definite could be obtained.

15 grams of the diazo compound, with 150 cc. methyl alcohol, partially dissolved; decomposition commenced at once, and proceeded slowly. After twenty-four hours it had ceased, but proceeded when the solution was warmed, and appeared to be complete after boiling for an hour. Distilled with steam, an oil separated, which was dried, weighed 7.5 grams, boiled at 131°–133°, and proved to be chlorbenzene, identical with that obtained in the last experiment. A small tarry residue was examined, without obtaining any other definite product.

o-Chlordiazobenzene Sulphate.—20 grams *o*-chloraniline yielded 24 grams of the diazo salt.

22 grams of the diazo compound dissolved in ethyl alcohol without decomposition. Warmed gently until decomposition had commenced it proceeded spontaneously, and developed so much heat that the flask and its contents had to be cooled by wiping it, from time to time, with a wet towel. The reaction was completed in about three-quarters of an hour, and it was then heated to boiling for half an hour. Aldehyde was given off during the reaction. Distilled with steam, an oil was separated, dried, and weighed 9 grams, and distilled over at 132°, showing the properties of chlorbenzene. No other definite product could be isolated.

25 grams of the diazo compound, with 200 cc. methyl alcohol, partially dissolved, decomposition beginning immediately, but proceeding very slowly. It was warmed from time to time, the decomposition being completed in about five hours. Distilled with steam an oil separated. It weighed 8.8 grams, distilled at 132°, and was identified as chlorbenzene. No other product could be isolated.

m-Chlordiazobenzene Nitrate.—20 grams *m*-chloraniline yielded 29.1 grams of the diazo salt.

25 grams of the diazo compound was decomposed with 200 cc. ethyl alcohol. Warming from time to time, the decomposition was completed in about three-quarters of an hour. Aldehyde was given off during the reaction. Distilled with steam an oil was separated, dried, weighed 9.1 grams, distilled at 132°–134°, and was identified as chlorbenzene. No other definite product could be isolated.

30 grams of the diazo compound, with 300 cc. methyl alcohol, partially dissolved with some decomposition, which had, however, not proceeded far after standing for sixty hours. It was then heated to boiling, and the decomposition was completed in an hour. On cooling, a voluminous, flocculent precipitate separated, which was filtered off and dried. It weighed 0.2–0.3 gram. It was but slightly soluble in alcohol or glacial acetic acid. The filtrate was distilled with steam, an oil separating, which was dried, weighed 12 grams, and distilled over, for the most part, at 187°–193°. A small residue of tarry material was examined, but yielded nothing definite.

m-Chlordiazobenzene Sulphate.—60 grams *m*-chloraniline yielded 110 grams of the diazo salt, a practically theoretical yield.

35 grams of the diazo compound, with 300 cc. ethyl alcohol, was warmed until decomposition had commenced, when it proceeded spontaneously, it being necessary to cool the flask by wiping it, from time to time, with a wet towel. The decomposition was completed in about an hour, aldehyde being given off during the reaction. Distilled with steam, an oil was separated, dried, weighed 15 grams, distilled over at 132°, and was identified as chlorbenzene. No other definite product could be isolated.

30 grams of the diazo compound, with 300 cc. methyl alcohol, partially dissolved and slowly decomposed. After standing sixty hours, it was necessary to boil for about two hours, to complete the decomposition. On cooling, a flocculent precipitate, apparently identical with the one obtained in the experiment described above, separated, was dried, and weighed

0.2 gram. The residue was distilled with steam, an oil was separated, dried, weighed 13 grams, and distilled, for the most part, at 187°–196°.

110 grams of the diazo compound, in two lots of 55 grams each, was decomposed with methyl alcohol, 300 cc. to each experiment. As in the last experiment, a flocculent precipitate separated after the decomposition was completed. It was filtered off, dried, and weighed 1.2 grams. The small quantity of this material, and its behavior toward solvents, prevented a further study of it. The filtrate was treated as in the last experiment, the greater portion of the oil distilling over at 187°-195°. No other definite products could be isolated. The three portions of oil, boiling above 186°, obtained from the decomposition of metachlordiazobenzene salts and methyl alcohol were now brought together, and subjected to fractional distillation. After four distillations, there was obtained a perfectly colorless, strongly refractive oil, possessing a peculiar, aromatic odor, and but faintly suggestive of anisol. It boiled constantly at 193°. It was analyzed for chlorine by the method of Carius.

Calculated for metachloranisol.	Found. I.	II.
24.88	25.18	25.12

p-Chlordiazobenzene Nitrate.—30 grams *p*-chloraniline yielded 36 grams of the diazo salt.

35 grams of the diazo compound, with 300 cc. ethyl alcohol, partially dissolved without decomposing. Heated to boiling, the decomposition was completed in about two hours. The alcohol was distilled off, and an oil precipitated from the distillate by adding water. The residue was distilled with steam, an oil coming over at first, followed by some light yellow material, which solidified in the condenser. The two portions of oil were brought together and distilled, commencing to come over at 132°, but the thermometer slowly rising. The latter portion of the distillate had an odor strongly suggestive of phenetol. The oil was probably chlorbenzene, containing a small quantity of *p*-chlorphenetol, but the quantity of material at disposal was too small to permit of a good separation. The solid material was dissolved in caustic potash,

filtered, evaporated to a concentrated solution, reprecipitated with hydrochloric acid, dried, and weighed 2 grams. After several recrystallizations from alcohol, it melted constantly at 87°, and was identified as chlornitrophenol of the formula $C_6H_3\left\{\begin{array}{ll} Cl & (1) \\ NO_2 & (3) \\ OH & (4) \end{array}\right.$. No other definite product could be obtained.

35 grams of the diazo compound, with 300 cc. methyl alcohol, partially dissolved without decomposition. After boiling for two hours the decomposition was completed. The alcohol was distilled off and an oil precipitated from it by adding water. The residue was distilled with steam, an oil coming over at first and then a solid material, as in the last experiment. The portions of oil (11 grams in all) were brought together, dried, and distilled, coming over at 200°. It was identified as *p*-chloranisol. The solid material was dried, and weighed 5.6 grams. This was dissolved in caustic potash, recrystallized, precipitated from a concentrated solution with hydrochloric acid, and recrystallized several times from alcohol, when it melted constantly at 87° and was identified as chlornitrophenol $C_6H_3\left\{\begin{array}{ll} Cl & (1) \\ NO_2 & (3) \\ OH & (4) \end{array}\right.$. No other definite product could be isolated from the residue.

p-Chlordiazobenzene Sulphate.—30 grams *p*-chloraniline yielded 55 grams of the diazo salt, a practically theoretical yield.

20 grams of the diazo compound with 200 cc. ethyl alcohol partially dissolved without decomposition. On warming, the decomposition commenced and then proceeded spontaneously, it being necessary to cool the flask by wiping it from time to time with a wet towel. The decomposition was completed in about an hour, and it was then boiled for half an hour longer. Distilled with steam, 9 grams of an oil was separated, dried, and redistilled, boiling at 132°. It was identified as chlorbenzene. Further examination of the residue yielded nothing definite. It was carefully examined for the presence of a sulphonic acid, but none was found.

50 grams of the diazo compound with 350 cc. methyl alcohol, partially dissolved without decomposing. Decomposition was completed after boiling for about five hours. Distilled with steam an oil was separated, weighing 15.4 grams. This was dried and distilled at 200°. It was identified as *p*-chloranisol. No other product could be isolated from the residue.

o-Bromdiazobenzene Nitrate.—30 grams *o*-bromaniline yielded 38 grams of the diazo salt.

15 grams of the diazo compound with 150 cc. ethyl alcohol partially dissolved with slight decomposition. Warmed until the decomposition was started, it proceeded spontaneously, it being necessary to cool the flask from time to time. The decomposition was completed in three-quarters of an hour. It was then boiled for a quarter of an hour. Aldehyde was given off copiously. Distilled with steam, an oil weighing 8 grams was separated, dried, distilled at 153°–154°, and was identified as brombenzene. No other definite product could be identified.

30 grams of the diazo compound with 300 cc. methyl alcohol, partially dissolved with slight decomposition. After boiling two hours the decomposition was completed. The alcohol was distilled off, and from it an oil precipitated by the addition of water. Distilled with steam, the residue yielded more oil. The two portions were brought together and dried. They weighed 12 grams. The oil distilled over at 153°-156°, and was then identified as brombenzene. No other definite product could be isolated.

o-Bromdiazobenzene Sulphate.—20 grams *o*-bromaniline yielded 31 grams of the diazo salt.

25 grams of the diazo compound with 250 cc. ethyl alcohol, partially dissolved without decomposition, even after standing several hours. Warmed until decomposition commenced, it proceeded spontaneously, the flask being cooled, from time to time, with a wet towel, to prevent too vigorous a reaction. The decomposition appeared to be complete in about a half hour. It was then boiled for a quarter of an hour longer. Distilled with steam, an oil was separated and dried. It weighed 10 grams, distilled at 154°, and was identified as brombenzene.

30 grams of the diazo compound, with 250 cc. methyl alcohol, partially dissolved, with slight decomposition, after standing an hour. It was then heated to boiling for five hours, when the decomposition was completed. Distilled with steam, an oil weighing 13 grams was separated and dried. It distilled at 154°, and was identified as brombenzene. A further examination of the residue yielded nothing definite.

m-Bromdiazobenzene Nitrate.—30 grams *m*-bromaniline yielded 34 grams of the diazo salt.

25 grams of the diazo compound, with 250 cc. ethyl alcohol, partially dissolved, with slight decomposition, after standing about 20 hours. Warmed until decomposition commenced, it proceeded spontaneously, and was completed in about three-quarters of an hour. It was then boiled for half an hour. Aldehyde was given off during the reaction. Distilled with steam an oil was obtained that weighed 11 grams and distilled over at 153°–156°. It was redistilled and identified as brombenzene. No other definite product could be isolated.

30 grams of the diazo compound with 250 cc. methyl alcohol, partially dissolved, with slight decomposition, after standing about twelve hours. Heated to boiling, the decomposition appeared to be complete in about an hour, and the boiling was continued for a half hour longer. On cooling, a voluminous flocculent precipitate separated which weighed 12 grams. On redistilling this oil the thermometer rose rapidly to 206°, and then slowly to 217°, by far the greater portion coming over between these figures (see next page). Further examination of the residue yielded nothing definite.

m-Bromdiazobenzene Sulphate.—30 grams *m*-bromaniline yielded 33 grams of the diazo salt.

25 grams of the diazo compound with 250 cc. ethyl alcohol, partially dissolved, with very slight decomposition, after standing twenty hours. Warmed until decomposition commenced, it proceeded spontaneously, and was completed in about an hour. It was then boiled for a half hour. Aldehyde was given off copiously. Distilled with steam an oil weighing 9 grams was obtained. It distilled entirely at 154°,

and was identified as brombenzene. No other product could be isolated.

30 grams of the diazo compound with 250 cc. methyl alcohol, partially dissolved, with slight decomposition, after standing twelve hours. Heated to boiling, the decomposition appeared to be complete in about an hour, but the boiling was continued for a half hour longer. On cooling, a voluminous, flocculent precipitate separated, which, when dried, weighed 0.15 gram. The filtrate was distilled with steam, when an oil weighing 11 grams separated. This was redistilled when about three-quarters of it came over at 207°–216°.

60 grams of the diazo compound with 300 cc. methyl alcohol, was decomposed, as in the last experiment. After cooling, the flocculent precipitate was filtered off, dried, and weighed 0.4 gram. It was brought together with the portion obtained in the last experiment, and unsuccessful attempts were made to crystallize it. The quantity of this material at disposal, and its conduct toward solvents, made a further study of it impossible.

The filtrate distilled with steam, yielded 20.5 grams of oil, which, for the most part, distilled over at 206°–217°. This portion was again distilled, yielding 15.5 grams of a colorless oil, strongly refracting, and with an odor strongly suggestive of the *m*-chloranisol, before described. It was analyzed for bromine by the method of Carius.

Calculated for *m*-bromanisol.	Found. I.	II.
42.7	44.6	44.5

The oil was again fractioned twice, and a portion, about 8 grams, was obtained, which distilled constantly at 214°, and was analyzed.

Calculated.	Found. I.	II.
42.7	43.5	43.6

It seemed probable that the substance was *m*-bromanisol, containing some brombenzene in solution, which could not be completely separated with the quantities at disposal. The residue was examined, but nothing definite obtained.

p-Bromdiazobenzene Nitrate.—40 grams *p*-bromaniline yielded 46 grams of the diazo salt.

55 grams of the diazo compound with 400 cc. ethyl alcohol, was boiled for about four hours, when the decomposition was completed. Aldehyde was copiously evolved. The alcohol was distilled off, and from it an oil separated on the addition of water. The residue was distilled with steam, an oil separating in the distillate. The two portions of oil were brought together, dried, and weighed 24 grams. It distilled at 154°, and was identified as brombenzene. No other definite product could be isolated.

20 grams of the diazo compound with 200 cc. methyl alcohol, partially dissolved, without decomposition. On gently warming, the decomposition proceeded evenly and was completed in about one and one-half hours. It was then boiled for twenty minutes. The alcohol was distilled off, and from it an oil precipitated by adding water. The residue was distilled with steam, an oil coming over at first and then a yellow, solid material. The portions of oil were brought together, dried, weighed 12 grams, and distilled at 220°–222°, being identified as *p*-bromanisol. The solid material was dissolved in caustic potash, recrystallized, and precipitated with hydrochloric acid. It weighed 1.5 grams. After crystallizing from alcohol it melted sharply at 88° and was identified as bromnitrophenol of the formula $C_6H_3\begin{cases}\mathrm{Br} & (1)\\ \mathrm{NO_2} & (3).\\ \mathrm{OH} & (4)\end{cases}$ No other definite product could be isolated.

p-Bromdiazobenzene Sulphate.—30 grams *p*-bromaniline yielded 39 grams of the diazo salt.

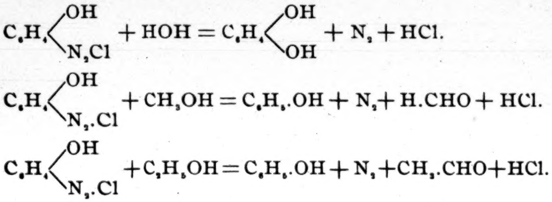
20 grams of the diazo compound with 200 cc. ethyl alcohol, was warmed until decomposition commenced, when it proceeded spontaneously, it being necessary to cool the flask, from time to time with a wet towel. The decomposition appeared to be complete in about three-quarters of an hour, and it was then boiled for twenty minutes longer. Aldehyde was evolved copiously. Distilled with steam 9 grams of an oil was obtained that distilled at 154°, and was identified as brombenzene. No other product could be isolated.

35 grams of the diazo compound with 300 cc. methyl alcohol, partially dissolved without decomposition. After boiling five hours the decomposition was completed. Distilled with steam, an oil was separated, dried, and weighed 14 grams. It distilled at 220°–223°, and was identified as *p*-bromanisol. No other definite product could be isolated.

SUMMARY.

The Diazophenols.

The experiments with the diazophenols here recorded are to be regarded as indecisive, as to the main object of this research. The only reactions that could be followed are expressed by these equations :



$$\mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{N_2Cl}\end{matrix}\right. + \mathrm{HOH} = \mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. + \mathrm{N_2} + \mathrm{HCl}.$$

$$\mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{N_2.Cl}\end{matrix}\right. + \mathrm{CH_3OH} = \mathrm{C_6H_5.OH} + \mathrm{N_2} + \mathrm{H.CHO} + \mathrm{HCl}.$$

$$\mathrm{C_6H_4}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{N_2.Cl}\end{matrix}\right. + \mathrm{C_2H_5OH} = \mathrm{C_6H_5.OH} + \mathrm{N_2} + \mathrm{CH_3.CHO} + \mathrm{HCl}.$$

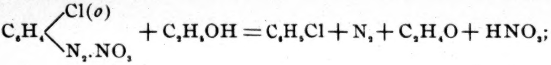
Or, in other words, the "oxy" reaction takes place, when a diazophenol is decomposed with water, and the hydrogen reaction with methyl or ethyl alcohol.

It does not seem probable that the alkoxy reaction took place to any extent, in any of the experiments described, because the products that would have been formed could have been readily recognized from their recorded properties.

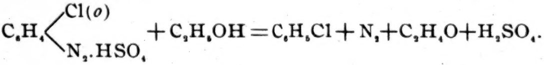
But it became evident in the course of the work on these substances that they are extremely unstable, very sensitive toward reagents, reacting themselves with the products of decomposition, so that secondary complicated reactions took place to such a degree as to modify and mask the expected reactions, if indeed, they took place at all. The main results are summarized below, and these results compared with others previously obtained.

The Chlordiazobenzenes.

Orthochlordiazobenzene salts with ethyl alcohol, as far as could be determined, gave the hydrogen reaction alone, as expressed by these equations :

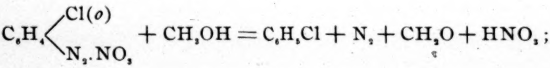


$$C_6H_4\left\langle\begin{matrix}Cl(o)\\N_2.NO_3\end{matrix}\right. + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + HNO_3;$$

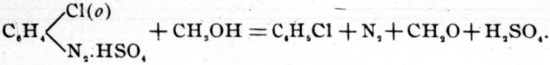


$$C_6H_4\left\langle\begin{matrix}Cl(o)\\N_2.HSO_4\end{matrix}\right. + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + H_2SO_4.$$

Orthochlordiazobenzene salts with methyl alcohol gave the hydrogen reaction alone :

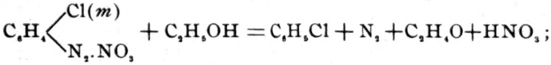


$$C_6H_4\left\langle\begin{matrix}Cl(o)\\N_2.NO_3\end{matrix}\right. + CH_3OH = C_6H_5Cl + N_2 + CH_2O + HNO_3;$$

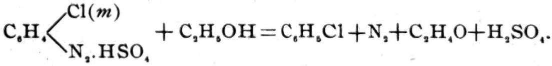


$$C_6H_4\left\langle\begin{matrix}Cl(o)\\N_2.HSO_4\end{matrix}\right. + CH_3OH = C_6H_5Cl + N_2 + CH_2O + H_2SO_4.$$

Metachlordiazobenzene salts with ethyl alcohol gave the hydrogen reaction only.

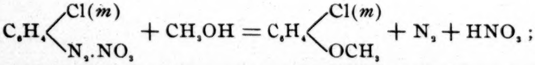


$$C_6H_4\left\langle\begin{matrix}Cl(m)\\N_2.NO_3\end{matrix}\right. + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + HNO_3;$$

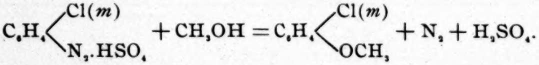


$$C_6H_4\left\langle\begin{matrix}Cl(m)\\N_2.HSO_4\end{matrix}\right. + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + H_2SO_4.$$

Metachlordiazobenzene salts with methyl alcohol gave more complicated reactions. The methoxy reaction apparently predominated, metachloranisol being the principal product :

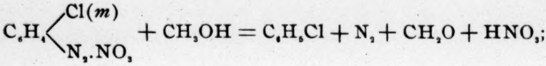


$$C_6H_4\left\langle\begin{matrix}Cl(m)\\N_2.NO_3\end{matrix}\right. + CH_3OH = C_6H_4\left\langle\begin{matrix}Cl(m)\\OCH_3\end{matrix}\right. + N_2 + HNO_3;$$

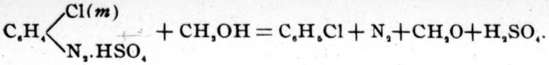


$$C_6H_4\left\langle\begin{matrix}Cl(m)\\N_2.HSO_4\end{matrix}\right. + CH_3OH = C_6H_4\left\langle\begin{matrix}Cl(m)\\OCH_3\end{matrix}\right. + N_2 + H_2SO_4.$$

At the same time it appeared that the hydrogen reaction took place to a slight extent :



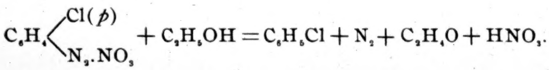
$$C_6H_4\begin{matrix}\diagup Cl(m)\\ \diagdown N_2.NO_3\end{matrix} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + HNO_3;$$



$$C_6H_4\begin{matrix}\diagup Cl(m)\\ \diagdown N_2.HSO_4\end{matrix} + CH_3OH = C_6H_5Cl + N_2 + CH_2O + H_2SO_4.$$

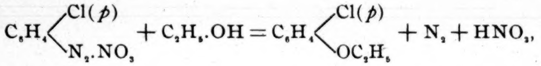
A small quantity of a well characterized solid was also formed, the nature of which was not determined.

Parachlordiazobenzene nitrate and ethyl alcohol gave principally the hydrogen reaction as expressed thus :



$$C_6H_4\begin{matrix}\diagup Cl(p)\\ \diagdown N_2.NO_3\end{matrix} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + HNO_3.$$

But at the same time, to no inconsiderable extent, the ethoxy reaction :



$$C_6H_4\begin{matrix}\diagup Cl(p)\\ \diagdown N_2.NO_3\end{matrix} + C_2H_5.OH = C_6H_4\begin{matrix}\diagup Cl(p)\\ \diagdown OC_2H_5\end{matrix} + N_2 + HNO_3,$$

accompanied by the formation of chlornitrophenol $C_6H_3\left\{\begin{matrix}Cl & (1)\\ NO_2 & (3)\\ OH & (4)\end{matrix}\right.$. The formation of a nitrophenol seems to be strictly analogous to the cases already carefully studied by Remsen and Orndorff,[1] of the action of diazobenzene nitrate on ethyl alcohol, and by Beeson[2] of the action of the diazo compound on methyl alcohol. From careful work on this point, these investigators concluded that the substance was formed by the elimination of nitrogen, and a molecular rearrangement of the diazo salt. Work done by Chamberlin[3] in this laboratory makes it appear probable that the alkoxy product is first formed, that this is then nitrated to some extent by the acid liberated in the reaction, and finally that the nitroether thus formed is saponified by boiling with the dilute acid, as in the formation of nitrocresols, from the nitration of cresol ethers, studied by Staedel.[4] I regret that circumstances prevented me from studying the nitration of chlorophenol ethers in this connection.

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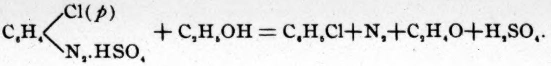
[1] This JOURNAL, **9**, 389.

[2] *Ibid*, **16**, 235.

[3] *Ibid*, **19**, 531.

[4] Ann. Chem. (Liebig), **217**, 158.

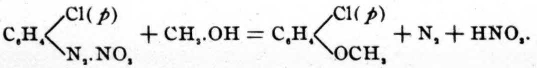
Parachlordiazobenzene sulphate and ethyl alcohol, as far as could be determined, gave only the hydrogen reaction :



$$C_6H_4\begin{cases}Cl(p)\\ N_2.HSO_4\end{cases} + C_2H_5OH = C_6H_5Cl + N_2 + C_2H_4O + H_2SO_4.$$

These last two experiments suggest, in a marked manner, what has been indicated by other work,[1] that the acid residue forming the salt of the diazo compound influences, to some degree, the nature of the reaction.

Parachlordiazobenzene nitrate and methyl alcohol gave the methoxy reaction entirely :

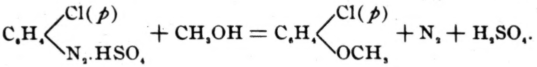


$$C_6H_4\begin{cases}Cl(p)\\ N_2.NO_3\end{cases} + CH_3.OH = C_6H_4\begin{cases}Cl(p)\\ OCH_3\end{cases} + N_2 + HNO_3.$$

At the same time some chlornitrophenol was formed,

$$C_6H_3\begin{cases}Cl & (1)\\ NO_2 & (3).\\ OH & (4)\end{cases}$$

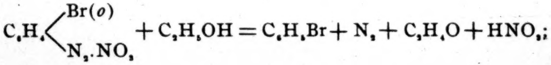
Parachlordiazobenzene sulphate with methyl alcohol gave the methoxy reaction alone :



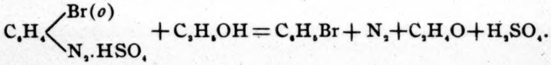
$$C_6H_4\begin{cases}Cl(p)\\ N_2.HSO_4\end{cases} + CH_3OH = C_6H_4\begin{cases}Cl(p)\\ OCH_3\end{cases} + N_2 + H_2SO_4.$$

The Bromdiazobenzenes.

Orthobromdiazobenzene salts with ethyl alcohol gave only the hydrogen reaction :



$$C_6H_4\begin{cases}Br(o)\\ N_2.NO_3\end{cases} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + HNO_3;$$



$$C_6H_4\begin{cases}Br(o)\\ N_2.HSO_4\end{cases} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + H_2SO_4.$$

Orthobromdiazobenzene salts with methyl alcohol gave only the hydrogen reaction :

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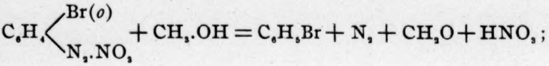
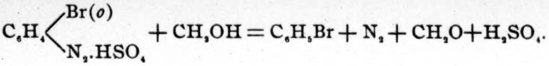
[1] Remsen and Graham : This JOURNAL, 11, 330.

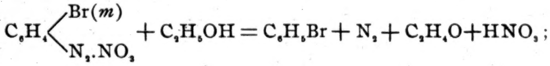


$$C_6H_4\Big\langle\begin{array}{l}Br(o)\\ N_2.NO_3\end{array} + CH_3.OH = C_6H_5Br + N_2 + CH_2O + HNO_3;$$

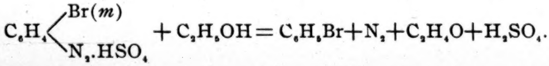


$$C_6H_4\Big\langle\begin{array}{l}Br(o)\\ N_2.HSO_4\end{array} + CH_3OH = C_6H_5Br + N_2 + CH_2O + H_2SO_4.$$

Metabromdiazobenzene salts with ethyl alcohol gave only the hydrogen reaction :

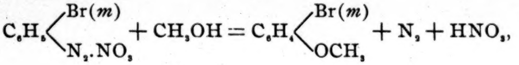


$$C_6H_4\Big\langle\begin{array}{l}Br(m)\\ N_2.NO_3\end{array} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + HNO_3;$$

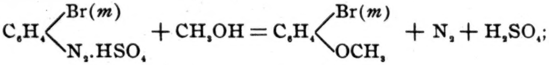


$$C_6H_4\Big\langle\begin{array}{l}Br(m)\\ N_2.HSO_4\end{array} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + H_2SO_4.$$

Metabromdiazobenzene salts with methyl alcohol gave principally the methoxy reaction :

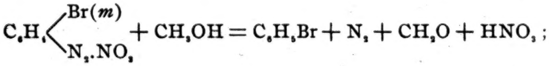


$$C_6H_5\Big\langle\begin{array}{l}Br(m)\\ N_2.NO_3\end{array} + CH_3OH = C_6H_4\Big\langle\begin{array}{l}Br(m)\\ OCH_3\end{array} + N_2 + HNO_3,$$

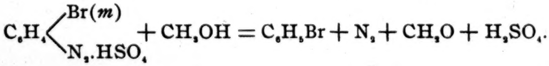


$$C_6H_4\Big\langle\begin{array}{l}Br(m)\\ N_2.HSO_4\end{array} + CH_3OH = C_6H_4\Big\langle\begin{array}{l}Br(m)\\ OCH_3\end{array} + N_2 + H_2SO_4;$$

and at the same time to an undetermined, but probably small extent, the hydrogen reaction took place :

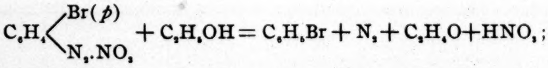


$$C_6H_4\Big\langle\begin{array}{l}Br(m)\\ N_2.NO_3\end{array} + CH_3OH = C_6H_5Br + N_2 + CH_2O + HNO_3;$$

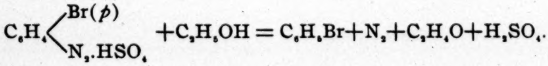


$$C_6H_4\Big\langle\begin{array}{l}Br(m)\\ N_2.HSO_4\end{array} + CH_3OH = C_6H_5Br + N_2 + CH_2O + H_2SO_4.$$

Parabromdiazobenzene salts with ethyl alcohol yielded only the hydrogen reaction :

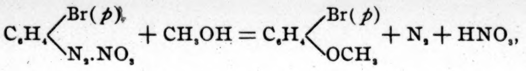


$$C_6H_4\Big\langle\begin{array}{l}Br(p)\\ N_2.NO_3\end{array} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + HNO_3;$$



$$C_6H_4\Big\langle\begin{array}{l}Br(p)\\ N_2.HSO_4\end{array} + C_2H_5OH = C_6H_5Br + N_2 + C_2H_4O + H_2SO_4.$$

Parabromdiazobenzene nitrate with methyl alcohol gave the methoxy reaction :

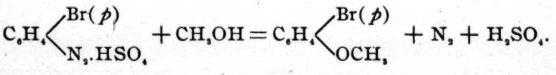


$$C_6H_4\begin{cases}Br(p)\\ N_2.NO_3\end{cases} + CH_3OH = C_6H_4\begin{cases}Br(p)\\ OCH_3\end{cases} + N_2 + HNO_3,$$

and at the same time was formed some bromnitrophenol,

$$C_6H_3\left\{\begin{array}{ll} Br & (1) \\ NO_2 & (3). \\ OH & (4) \end{array}\right.$$

Parabromdiazobenzene sulphate with methyl alcohol yielded the methoxy reaction alone :



$$C_6H_4\begin{cases}Br(p)\\ N_2.HSO_4\end{cases} + CH_3OH = C_6H_4\begin{cases}Br(p)\\ OCH_3\end{cases} + N_2 + H_2SO_4.$$

CONCLUSIONS.

There are now, excluding the diazophenols, five cases available for comparison, and the discussion of the primary objects of this investigation, the decomposition with water, methyl and ethyl alcohol, of diazobenzene, diazobenzoic acids, chlordiazobenzenes, bromdiazobenzenes, and the nitrodiazobenzenes.

It has seemed to me better, on the whole, to discuss these cases together, and to facilitate this, I have tabulated the results of the experiments with methyl and with ethyl alcohol. There is no reason to believe that in any of these cases, the reaction with water would be otherwise than normal, so that the reaction with it need not be included.

With Methyl Alcohol.

	Ortho.	Meta.	Para.
Diazobenzene		Methoxy entirely	
Diazobenzoic acid	Methoxy	Methoxy	Methoxy
Chlordiazobenzene	Hydrogen	Methoxy in excess of hydrogen.	Methoxy
Bromdiazobenzene	Hydrogen	Methoxy in excess of hydrogen.	Methoxy
Nitrodiazobenzene	Hydrogen	Hydrogen and methoxy in traces.	Hydrogen and methoxy 8%.

With Ethyl Alcohol.

	Ortho.	Meta.	Para.
Diazobenzene	Ethoxy in excess of hydrogen		
Diazobenzoic acid	Hydrogen	Hydrogen in excess of ethoxy.	Ethoxy
Chlordiazobenzene	Hydrogen	Hydrogen	Hydrogen in excess of ethoxy.
Bromdiazobenzene	Hydrogen	Hydrogen	Hydrogen
Nitrodiazobenzene	Hydrogen	Hydrogen	Hydrogen

A study of all the facts indicated by these tables seems to me to warrant the following conclusions:

1. The alkoxy reaction is normal, and the hydrogen reaction, when it takes place, is a modification induced by special conditions.

2. Regarding water as the first member of the series, the more complex the alcohol, the greater the tendency towards the hydrogen reaction. This is in accordance with the view expressed by Metcalf.[1]

3. That acid radicals, as COOH, Cl, Br, NO_2, etc., induce the hydrogen reaction, and their influence in this respect is probably in the order in which they are here named. This is in accordance with the views expressed by Remsen and Graham,[2] from a study of all the cases on record in which these radicals occur.

4. That the presence of the substituting radical in the ortho position is most favorable to the hydrogen reaction, and the meta position more favorable than the para.

REVIEWS.

LABORATORY EXPERIMENTS ON THE CLASS REACTIONS OF ORGANIC SUBSTANCES AND THEIR IDENTIFICATION. By ARTHUR A. NOYES, PH.D., Assistant Professor of Organic Chemistry in the Massachusetts Institute of Technology, and SAMUEL P. MULLIKEN, PH.D., Instructor of Organic Chemistry in the Massachusetts Institute of Technology. Easton, Pa.: Chemical Publishing Co. 1897. 28 pp. Price 50 cents.

The object of this book is clearly stated in the title. To quote from the preface of the authors: "Experience has shown that the preparation of typical organic substances in accordance with the plans followed in the manual of Gattermann, Levy, Fischer, etc., teaches satisfactorily the manipulative methods of organic chemistry and the manner of execution of the leading synthetic processes, but that it fails to a surprising extent in the case of most students to give a knowledge of the important characteristics of the various classes of organic compounds, and therefore of the fundamental principles of the science. Unless an instructor is continually on the alert, the course of preparation work becomes almost inevitably a routine following the direction." The last sentence must go straight to the heart of every teacher who has tried to deal conscientiously with his students. That dreadful tendency to get in a rut, to work mechanically, to let the fingers move without any accompanying action of the mind, is known to us all. The only way in which it can possibly be mitigated—it cannot be prevented entirely—is to have an instructor "continually on the alert." No scheme, written, or printed, or spoken, can do anything like as much as the living teacher at the elbow of the worker.

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[1] This JOURNAL, 15, 301.

[2] *Ibid*, 11, 331.

There are, however, books that drive one into a routine at once, and others that do not, and any book of the latter character must be helpful in a laboratory. This little work of Messrs. Noyes and Mulliken belongs to the second class and will be of service. It is made up of three parts.

Part I deals with experiments illustrating the class reactions of organic compounds; detection of water in organic compounds; the reactions distinguishing double and triple-bonded from single-bonded compounds; the reactions of triple-bonded compounds; the behavior of hydrocarbons in general; the reactions of compounds containing the hydroxyl group; the reactions of alcohols and phenols; the reactions of organic acids; the reactions of aldehydes, etc.

Part II deals with experiments illustrating the methods of detection of nitrogen, sulphur, and halogens in organic compounds; and Part III with the identification and separation of unknown organic substances.

I. R.

PRACTICAL EXERCISES IN ELECTROCHEMISTRY. By DR. FELIX OETTEL. Translated (with the author's sanction) by EDGAR F. SMITH, Professor of Chemistry in the University of Pennsylvania. Philadelphia, Pa.: P. Blakiston, Son & Co. 1897. 92 pp.

This little book is intended to furnish chemical students with directions for a brief course of experiments in the application of electrochemical methods to chemistry. The first part deals with the sources of current, regulators, measuring apparatus, and methods of dealing with the current in general. Among the experiments illustrating the application of electrical methods to chemical reactions are the formation of hypochlorites and chlorates; the electrolysis of hydrochloric acid without a diaphragm; the electrolysis of sulphuric acid;

the electrolysis of a salt solution with use of a diaphragm; the use of hydrochloric acid with a diaphragm ; the formation of persulphuric acid by electrolysis of sulphuric acid ; the preparation of magnesium ; the electrolysis of fused lead chlorate; the electrolysis of sodium acetate ; the reduction of nitrobenzene to azobenzene, etc.

An advanced student in chemistry who has the time at his disposal would do well to perform a number of these experiments. This branch of chemistry is coming more and more into prominence, and it is well to get at least a glimpse of the methods that are in use. It may fairly be assumed that the methods described are well described and that the translation is well done.

I. R.

TEXT-BOOK OF PHYSICAL CHEMISTRY. By CLARENCE L. SPEYERS, Associate Professor of Chemistry, Rutgers College. New York: D. Van Nostrand Company. pp. 224. 1897.

The subject is treated primarily from the standpoint of energy. In his preface the author says: "I have adopted the view that matter is a collection of energies in space, considering the relations of the energies to be the prime object of investigation. With Ostwald, I feel confident that the materialistic interpretation has passed its prime, and has no promise for the future."

The various manifestations of energy are taken up first, while volume energy is dealt with more fully in the chapter on gases. The fundamental laws of thermodynamics are discussed under the heading, Heat. Various properties of solutions, such as Osmotic Pressure, Vapor Pressure, etc., are considered under the title, Physical Changes. In this same part of the book, the work on Molecular Weight of Liquids is also taken up. In the chapter on Equilibrium we find a mathematical discussion of the Conditions of Equilibrium, Equilibrium in Gaseous, Liquid, and Solid Systems, also in Solid-gas, Liquid-gas, and Solid-liquid Systems. A brief treatment of Chemical Kinetics gives the equations for what are termed monad, diad, and triad reactions, and the chapter on Phases, treats of the Conditions of Equilibrium, Monad, and Diad Systems.

The last fourth of the book is devoted to the important and interesting subject of Electrochemistry, including the Laws of the Current, the Ionic Condition in Solution, the Conductivity of Solutions, the Migration Velocity of the Ions, the Source of the Potential in Primary Cells, the Gas Battery, Polarization, Constant Cells, etc., and a few pages are devoted to Electrolytic Separations, and Electrochemical Analysis.

The book concludes with a very brief account of the general properties of ions, and the modes of their formation.

H. C. J.

MANUEL D' ANALYSE CHIMIQUE APPLIQUÉE À L' EXAMEN DES PRODUITS INDUSTRIELS ET COMMERCIAUX. Par Émile Fleurent. Paris: Georges Carré et C. Naud. 1898. pp.582.

This work proposes to give, chiefly for the use of those practically concerned with chemical industry, a condensed account of the general methods of inorganic analysis—qualitative and quantitative—and of elementary organic analysis, and a selection of special methods (in most cases but one of each kind—it would have been well to add at least references to others) for the examination of the principal raw materials and products which the chemist is called upon to investigate.

It may be feared that in the first or general part the aim of the author, to condense a large subject into as small a space as possible, has rendered the book of little use to a beginner, or to anyone trusting to this as his only guide—many important details, precautions, and references to possible complications being omitted—while the very general directions given are needless in the case of one who has already practically studied the subject with the aid of one of the more extended treatises.

The same remarks may be made in regard to the inorganic division of the special part of the work. For example, about two pages only are given to the determination of silver in its ores, including cupellation; fuel is disposed of in less than two pages; and about three and a half pages are devoted to the analysis of wrought and cast iron and steel. There are brief but sensible suggestions as to the taking of samples, a matter often less carefully considered than its real importance demands.

Some of the subjects in the organic division of the special part are treated of in much more detail, and are likely to be of much more use to practical workers in the laboratory. This is true of the chapters on fats and oils (methods in use in the *Laboratoire Municipal de Paris*) on butter and its adulterants (method of Müntz), on beet-sugar, its by-products and related materials, on grapes and other fresh fruits (method of Aimé Girard and Lindet), on wine, distilled spirits (notice of the estimation of furfural), determination of acetone in crude wood-spirit and "denaturalized" alcohols, etc. The methods given are for the most part those of French chemists, and in some instances deserving of special attention; in other cases valuable processes which have been worked out elsewhere, are unduly neglected and passed over without notice.

Some important subjects are altogether omitted, for instance the chemical examination of explosives. The printing is clear and good, and there are neat illustrative engravings. There is a table of contents, but no alphabetic index, as is so often the case with books published in France.

J. W. M.

THE PRINCIPLES OF CHEMISTRY. By D. MENDELÉEF. Translated from the Russian (sixth edition) by GEORGE KAMENSKY, A.R.S.M., of the Imperial Mint, St. Petersburg, Member of the Russian Physico-Chemical Society. Edited by T. A. LAWSON, B.Sc., Ph.D., Examiner in Coal-tar Products to the City and Guilds of London Institute, Fellow of the Institute of Chemistry. In Two Volumes. Longmans, Green & Co., 39 Paternoster Row, London, New York, and Bombay. 1897. Vol. I., 621 + xviii pp. Vol. II., 518 pp. 8vo. Price $10.00.

When the first German edition of this book appeared in 1891, a review of it was published in this Journal (Vol. **13**, p. 139), which closed with the following words: "Every teacher and every advanced student of chemistry should read and study this book with care. Even the most experienced teacher will find much in it that will prove of value to him."

At the present time, the book is so well known that a review of this new edition may be regarded as superfluous. Of course the new is better than the old edition. It has been carefully brought up to date. Argon and helium, hydrazine and hydronitrous (triazoic) acid, the nitrides and carbides which Moissan has brought into such prominence during the last few years, all of these are treated of—some very fully, others meagerly. It matters little, however, whether one or another compound may have been overlooked, the book is not intended for reference, but for study, and to this it is admirably suited, not certainly on account of its orderliness, for there are few books on chemistry less orderly, but on account of the spirit that breathes through it, and that stimulates the student, young or old. It is thoughtful, and therefore helpful. The author has his own ideas on all subjects, and he seems to be at the side of the reader with some valuable suggestion, no matter how apparently trivial the particular subject may be which is under treatment.

In regard to the original sixth edition, of which the book before us is a translation, the author says: In this the sixth edition I have not altered any essential features of the original work, and have retained those alterations which were introduced into the fifth edition. I have, however, added many newly-discovered facts, and in this respect it is necessary to say a few words. Although all aspects of the simplest chemical relations are as far as possible equally developed in this book, yet on looking back I see that I have, nevertheless, given most attention to the so-called indefinite compounds, examples of which may be seen in solutions. I recur repeatedly to them, and to all the latest data respecting them, for in them I see a starting-point for the future progress of our science, and to them I affiliate numerous instances of indefinite compounds, beginning with alloys and silicates, and ending with complex acids. * * * My own view is that a solution is a homogeneous liquid system of unstable dissociating compounds of the solvent with the substance dissolved. * * At present, my ideas respecting solutions are shared by few, but I trust that by degrees the instances I give will pave the way for their general recognition." I. R.

CORRESPONDENCE.

WASHINGTON, D. C., FEBRUARY 14, 1898.

Editor of the American Chemical Journal:

Dear Sir.—The Organization Committee of the Third International Congress of Applied Chemistry which is to be held in Vienna during the coming summer, has fixed the date of the meeting from July 28, to August 2, 1898. Some time during the month of February, programs and announcements will be sent to all persons who have been enrolled as members of the Congress.

Respectfully,
H. W. WILEY,
Chairman of the American Committee.